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TECH BRIEF 68-10557

IMPROVED SEPARATORS FOR SILVER OXIDE-ZINC AND SILVER OXIDE-CADMIUM CELLS FOR SPACECRAFT APPLICATIONS

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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Technology Utilization Division
OFFICE OF TECHNOLOGY UTILIZATION
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
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Research originally conducted on improved separators resulted in materials whose use extended cell life five-fold and prevented catastrophic shorting due to zinc dendrite growth. The further development of membranes suitable for use in alkaline cells such as secondary silver-zinc or silver-cadmium cells has resulted in improved performance, the best of which was exhibited by membranes comprised of methyl cellulose as the chief component.

New membranes which passed certain preliminary screening tests at The Borden Laboratories were tested under sub-contract by Electric Storage Battery Company using simplified three-plate silver zinc oxide cells in a standard cycling test. The entire E.S.B. final report is included as Appendix to the present report. Based on the findings of the cycle tests, separator materials were chosen for the silver-zinc cells required under contract. Additional materials have been recommended for similar research.

The information in this Technical Support Package comprises the documentation announced in NASA Tech Brief 68-10557 and is provided under the Technology Utilization Program of the National Aeronautics and Space Administration to make available the results of aerospace-related developments considered to have wider technological, scientific or commercial applications. These studies derive from the Technology Utilization Program managed by NASA's Goddard Space Flight Center. Mr. Thomas J. Hennigan, NASA Liaison Officer of this project, was particularly helpful in bringing the viewpoint of the electrical engineer into focus with the other disciplines used in this study. The Final Report was written by Helmuth L. Pfluger and Howard E. Hoyt, in conjunction with contract development by The Borden Chemical Company. The writers were assisted at The Borden Chemical Company by Dr. George Kitazawa, Head of the Physical Testing Laboratory, Mr. Richard Trickey, Chemist and by Messrs. R. G. Burton, S. Weeks, A. Maiter, E. Arnold and W. Morris, Assistants. At the Carl F. Norberg Research Center of the Electric Storage Battery Company, the sub-contract tests were supervised by Mr. J. J. Kelley, Manager of Polymeric Materials Division.

Additional information regarding Improved Cell Technology may be found in Scientific and Technical Aerospace Reports (STAR) which is a comprehensive abstracting and indexing journal covering worldwide report literature on the science and technology of space and aeronautics. STAR is available to the public on subscription from the Superintendent of Documents, U. S. Government Printing Office.

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IMPROVED SEPARATORS FOR SILVER OXIDE-ZINC AND SILVER OXIDE-CADMIUM CELLS FOR SPACECRAFT APPLICATION

by

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and
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July, 1967

Prepared for

Goddard Space Flight Center

Contract NAS 5-9107

Modification 6

The Borden Chemical Company
Central Research Laboratory
Philadelphia, Penna. 19124

SUMMARY AND CONCLUSIONS

1) On the basis of screening tests at Electric Storage Battery Company, materials judged worthy of further evaluation singly in full cells are:

For use in 30-40% potassium hydroxide

	Parts by weight	
5-9107-21	100	methyl cellulose
	9	potassium hydroxide
5-9107-22	90	methyl cellulose
	10	PVM/MA
	28	potassium lactate
5-9107-27	100	methyl cellulose
	10	tetramethyl ammonium hydroxide
5-9107-29		Polyvinyl alcohol, type 42-88

For use in 45% potassium hydroxide

	Parts by weight	
5-9107-23	100	methyl cellulose
	33	potassium acetate

2) Also on the basis of the E.S.B. screening tests, evaluation in full cells should be made on several combinations of two types of membrane, the one type stopping silver ion by reducing it to metallic silver, the other type permitting small amounts of silver ion to diffuse but being very resistant to zinc. Promising examples of such alternating combinations in the E.S.B. tests were:

Oxidizable Type		Oxidation-resistant type Parts by weight	
5-9107-29	100 Polyvinyl Alcohol 42-88	C3	(70 methyl cellulose 30 PVM/MA)
5-9107-29	100 Polyvinyl Alcohol type 42-88	5-9107-23	(100 methyl cellulose 33 potassium acetate)
5-9107-30	95 Polyvinyl Alcohol type 42-88 5 PVM/MA	5-9107-27	(100 methyl cellulose 10 tetramethyl ammonium hydroxide)
5-9107-33	100 Polyvinyl Alcohol 30-98	C3	(70 methyl cellulose, 30 PVM/MA)

3) The silver-zinc cells called for by this Contract are being made at Electric Storage Battery Company (Raleigh Missile Division) using as separator materials, chose from the above candidates, 5-9107-27 (methyl cellulose-tetramethyl ammonium hydroxide) at 1.5 mils, 5-9107-29 (polyvinyl alcohol 42-88) at 1.5 mils, and combination wrap of the two in alternating 0.7 mil layers. These will be compared against C3 films on which there is now a substantial amount of test data available.

4) If 5-9107-27 should have cycle-life at all comparable with C3, it would have an advantage over C3 because it is more flexible at the same relative humidity and would therefore be easier to handle during cell assembly.

5) The pin-pointed tests will evaluate the relative merits of respectively an oxidizable membrane, an oxidation-resistant membrane and a double layer containing both.

6) The new wrapping technique chosen for application of the double layer is to superimpose thin sheets of the two separator types, then U-wrap with the double layer as though it were a single sheet.

7) The classification of separators into oxidizable and non-oxidizable types stems from silver diffusion tests reported in detail in the Second Progress Report and included in full as Appendix I of this report. Oxidizable films are initially very effective barriers to silver but they are degraded by the oxidation and prone to eventual catastrophic damage. Non-oxidizable films which retard silver ion diffusion retard also the passage of KOH electrolytes. Therefore conductivity is increased at the expense of a finite rate of silver-diffusion. It is therefore pertinent to compare the relative merits of superior examples of the two types, alone and in combination. Particular interest attaches to the outcome of experiments in which the cells are permitted to stand in a charged condition for extended periods of time.

8) The electrolytic conductivity of membranes comprising methyl cellulose can be increased as much as one hundred-fold by pre-swelling either at low temperatures in the same concentration of potassium hydroxide or at room temperature in lower concentrations of potassium hydroxide. It is recommended that the parameters of these pre-swelling treatments be given further study and that representative pre-swollen films be tested in cells.

9) One way of exploiting the pre-swelling techniques is to assemble the cell first, wrapping the electrode with untreated dry methyl cellulose film, then carry out the pre-swelling step in the assembled cell.

10) Using pre-swelling treatments on methyl cellulose compositions containing polar additives such as polyacids or salts of organic acids, extremely low resistances were obtained - below those of cellophane. Since silver diffusion rates are correspondingly increased, such membranes are more likely to be of value where long periods of stand in the charged (silver oxide) state are not required, or in systems combining them with adequate layers of silver-scavenging film.

11) Screening tests were made on two types of synthetic membranes, namely methacrylic ester-acrylic acid copolymers and polyvinyl pyridine-polyacid co-acervates. Both types were found oxidation-resistant and within a useful electrolytic resistance range. At the particular stage in their development both types were also lower in flexibility and strength than films based on methyl cellulose.

12) Treatment of polyethylene and modified polyethylene (Surlyn) films by swelling-leaching procedures increased conductivity by several orders of magnitude but insufficiently to be of practical interest.

13) Preliminary studies explored the possibilities of constructing envelopes for the zinc electrode using materials of the present Contract. Results in cells were not definitive but indicated that this approach merits further experimental effort.

DATA & DISCUSSION

A. Cell Tests at Norberg Research Center, E.S.B.

The Norberg Research Center employed a rapid screening method for testing experimental separators in cells. This was accomplished by limiting the separator thickness to two layers, the cell stack to only three plates, and using a cycling regime which included discharge at 100% depth and 20% overcharge in each cycle. The regime included also an accelerated charged stand test of two weeks at 45° C.

Compositions and properties of the materials submitted to E.S.B. are summarized in Tables I and II. The last four items in Table I are separator envelopes constructed in various ways as described under section H, using polyvinyl alcohol with and without C3 either on a viscose substrate or unsupported and heat sealed. Mr. J. J. Kelley's final report of the cycle tests is attached to this report in its entirety.

Table I. - Description and Properties of Films Tested at Electric Storage Battery Company in Three-Plate Ag-ZnO Cells (see also Table II)

NAS 5-9107	Lot No.	Composition (in parts by weight)	Dry Thickness (mils)	MIT (b) Flex Cycles	Tensile psi	Tensile Extension %
21	522-62	100 Methyl Cellulose 9 Potassium Hydroxide	1.5	1,920	7,190	40
22	522-119	90 Methyl Cellulose 10 PVM/MA 28 Potassium Lactate	1.6	7,926	4,780	42
23	534-63	100 Methyl Cellulose 33 Potassium Acetate	1.5	7,311	4,320	47
24	534-43	100 Methyl Cellulose 17 Potassium Acetate	1.5	7,184	4,860	45
25	504-6	80 Methyl Cellulose 20 PVM/MA 10 Hydroxypropylamine	1.5	5,422	7,110	31
26	545-18 534-24	50 Methyl Cellulose 50 PVM/MA 25 Polyvinyl Alcohol	1.4	779	15,000	7
27	545-64	100 Methyl Cellulose 10 Tetramethyl Ammonium Hydroxide	1.5	5,295	6,640	26
28	545-116	100 Methyl Cellulose 32 Potassium Succinate	1.5	1,277	3,760	20
29	563-101	100 Polyvinyl Alcohol 42-88	1.5	>20,000	11,000	210
30	563-115	95 Polyvinyl Alcohol 42-88 5 PVM/MA	1.5	10,000	12,400	8
31	563-156	70 Methyl Cellulose 30 PVM/MA 5 Triethanolamine	1.5	6,657	-	-
32	563-157	70 Methyl Cellulose 30 PVM/MA 5 Triethyleneglycol	1.3	3,512	-	-
33	574-9	100 Polyvinyl Alcohol 30-98	0.7	> 20,000	-	-
33	499-65	100 Polyvinyl Alcohol 30-98	1.6	>20,000	11,000	360
2	499-15	70 Methyl Cellulose ("C3" 30 PVM/MA)	1.5	754	14,700	9
		Cellophane (PUDO)	1.0	>20,000	-	-
		SEPARATOR ENVELOPES (a)				
	563-46	Polyvinyl Alcohol 42-88 on Viscose	6.0			
	563-47	Polyvinyl Alcohol/ "C3" on Viscose	6.0			
	545-65	Polyvinyl Alcohol on Viscose	6.0			
	563-56	Polyvinyl Alcohol/"C3" Unsupported, heat sealed	4.1			

(a) The construction of these envelopes is described on page 25.

(b) ASTM Test D643-43, at 200 g. tension and 50% R.H.

Table II. - Properties of Films Tested at Electric Storage Battery Company in Three-Plate Ag-ZnO Cells (Continued from Table I)

NAS 5-9107	Dry mil	Resistance - ohms-cm 30% KOH	45% KOH	30% KOH ZnO at CRL	31% KOH-ZnO at ESB	45% KOH-ZnO at CRL	45% KOH-ZnO at ESB	Swell Ratio 30% KOH	Swell Ratio 45% KOH	Arbitrary[a] Silver ion Transfer Factor 30% KOH
21	1.5	55.0	282.	83.3	118.4	466.	-	1.33	1.28	(8.2)
22	1.6	26.7	66.9	38.0	54.2	243	-	1.35	1.37	7.4
23	1.5	28.1	78.6	41.8	18.1	364.	-	1.20	1.16	7.5
24	1.5	43.9	94.5	56.7	61.1	-	-	1.22	1.10	8.9
25	1.5	17.5	484		28.0	-	-	1.52	1.51	-
26	1.4	8.9	61.8	8.9	12.7	-	-	2.0	2.14	15.3
27	1.5	29.2	46.7	29.4	59.1	141	-	1.27	1.32	10.7
28	1.5	15.1	36.7	(13.8)	-	-	36.5	1.39	1.28	15.8
29	1.5	21.1	29.0	35.2	19.8	37.0	-	1.74	2.20	2.1
30	1.5	16.3	18.2	22.0	15.4	32.9	-	1.94	2.47	2.7
31	1.5	16.2	30.5	-	-	30.5	36.4	(1.60)	(1.60)	-
32	1.3	16.5	21.5	-	40.7	28.7	40.7	(1.60)	(1.60)	-
33	0.7	16.7	18.3	-	-	-	-	1.92	2.47	-
33	1.6	18.8		27.9	-	46.5	-	1.92	2.47	3.0
C3	1.5	18.0	474	18.0	20.7	617.	-	1.70	1.70	8.3
PUDO	1.0	5.9	9.8	8.3	8.7	16.1	-	3.30	3.0	-

CRL denotes measurements at Central Research Laboratories, The Borden Chemical Company.

ESB denotes measurements at Carl F. Norberg Research Center of the Electric Storage Battery Company.

(a) The arbitrary transfer factor is defined on page 6 of Appendix I of this report.

B. Modification of Methyl Cellulose-Polyacid Films with Bases

Methyl cellulose-polyacid films have low electrolytic resistance in 30% KOH and have performed well in test cells. These compositions, however, are less flexible than unmodified methyl cellulose. For example, Film C3 (70 parts methyl cellulose, 30 parts PVM/MA, the 1:1 copolymer of vinyl methyl ether and maleic anhydride) has demonstrated improved performance in a substantial amount of test data,[a][b] but it must be handled with care at 50% R.H. in order to avoid possibility of cracking during assembly of cells. Methyl cellulose-polyacid films also have excessively high resistance in 45% KOH.

The addition of organic amines to methyl cellulose-polyacid compositions was extensively explored during the third quarter of the previous contract.[c] The observed improvement in conductivity could be attributable severally to salt formation with the polyacid, to enhancement of polarity by the amine group or to extraction of the bulky amine by the cell liquid filling a greater volume of film interstices with conductive solution. It was therefore of interest to compare an organic base with potassium hydroxide at levels roughly corresponding to equal degrees of salt formation or buffering. This was done by adding to the 10% aqueous solution of the polymers sufficient of each base to bring the solution to the same pH (within 0.1 unit). The polymer composition selected for the experiment was B3.3 (33% polyacrylic acid, 67% methyl cellulose) and the organic base was 3-hydroxypropylamine.

Data on electrolytic resistance of films swollen in 45% KOH are summarized in Table III. It appears that the organic base is more effective than KOH in lowering the resistance at equal degrees of salt formation initially in the dry film. However, the decrease in resistance is about the same on a weight percent basis regardless of whether the base is hydroxypropylamine or KOH, as is evident from the plot in Figure 1. These facts strongly suggest that on equilibration with electrolyte the amine may be replaced by a roughly equal weight of KOH.

(a) T. J. Hennigan, Goddard Space Flight Center Report X-716-65-331 (1965).
(b) T. J. Hennigan, private communication.
(c) H. L. Pfluger and H. E. Hoyt, Final Report, NAS-9107, pp. 4-10.

Under the conditions used for testing film conductivity, hydroxypropylamine (HPA) and triethanolamine are essentially completely removed from the methyl cellulose-polyacid films while they are being equilibrated in a large excess of agitated electrolyte solution prior to being introduced into the conductivity cell. After equilibration, blotted films have shown zero nitrogen content by Kjeldahl analysis. Complete extraction has also been demonstrated under conditions of no agitation in a Petri dish with electrolyte/film ratio equal to 25.

The question arises as to how close these conditions of complete extractability correspond to the conditions of the battery cell. With this in mind, an experiment was made with initial ratio of electrolyte to film equal to 6.3. This was accomplished by using two polyethylene forms having the dimensions of electrodes. The forms were U-wrapped with five turns of C2A film (C2 containing 10% HPA on polymer), packed tightly with polyethylene shims into a battery cell and covered with 30% KOH. After three days, the wrapped electrolyte forms were removed and unwrapped. The blotted film was submitted to Kjeldahl analysis for nitrogen. An unsoaked film of the same dimension was analyzed by the same method. The results indicated that only about 35% of the amine was extracted by the electrolyte. In commercial cells having lower electrolyte/film ratio, extraction might be still lower.

TABLE III. - Comparison of Hydroxypropylamine With Potassium Hydroxide as Modifiers of B3.3 Film

Reference	pH (a)	Percent (b) Base Added KOH	Amine	Film Properties Thickness (mils)	Resistance milliohms-cm^2 (c)	MIT Flex (Cycles) (d)
421-113	2.8	0	0	1.5	315	(308)
504-18	3.5	1.8	-	1.6	367	1229
504-16	4.0	3.4	-	1.6	200	1688
504-19	4.1	-	5.3	1.4	134	1682
504-15	4.4	5.3	-	1.4	97	1747
504-23	4.4	-	7.5	1.4	40	2757
509-17	5.1	10.8	-	1.7	47	232
504-24	5.0	-	14.4	1.6	14	4958
504-25	6.1	-	25.0	1.8	11	1311

(a) pH of a 10% aqueous solution of polymer mixture containing 33 parts by weight polyacrylic acid and 67 parts methyl cellulose, after addition of stated amount of base.

(b) Weight percent of polymer solids.

(c) Electrolytic resistance of film swollen in 45% KOH.

(d) ASTM Folding Endurance Test for Paper, D643-43; 200 g. tension on film conditioned at 50% R.H.

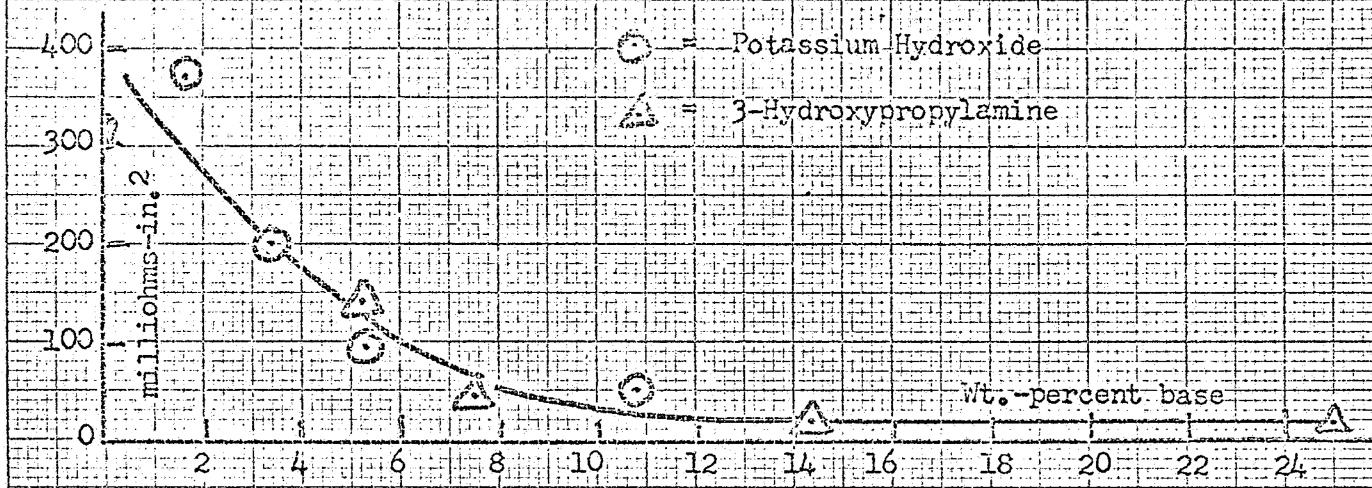


Fig. 1. Effect of Base on Resistance of B3.3 Film

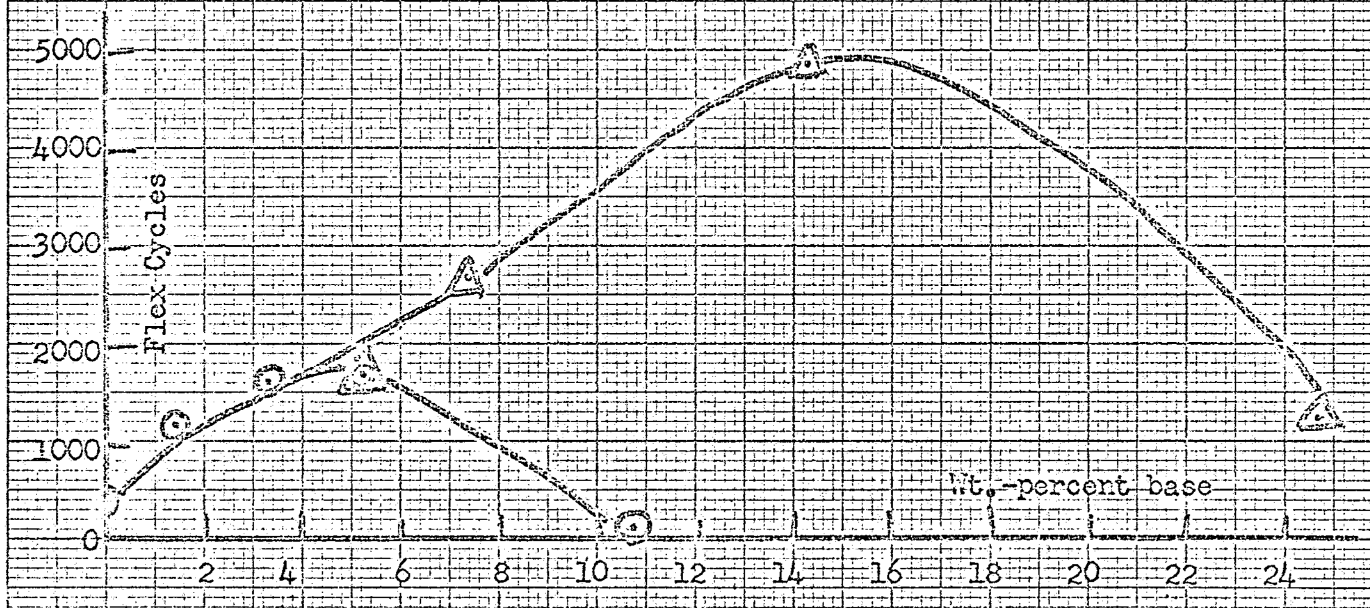


Fig. 2. Effect of Base on Flex of B3.3 Film

= Potassium Hydroxide

= 3-Hydroxypropylamine

Also included in Table III are the results of flex tests, which show that up to pH 4, KOH and hydroxypropylamine flexibilize to a small and equal degree. When higher amounts of the bases are added, the amine flexibilizes more than KOH. This is also shown in Figure 2 in which flex is plotted against weight-percent of base. With proportions above six weight-percent, and up to about 15%, it is more advantageous to use hydroxypropylamine instead of KOH even though both bases result in the same low electrolytic resistance: in this concentration range, KOH tends to embrittle the film whereas hydroxypropylamine, to the contrary, flexibilizes quite efficiently.

Experiments in which triethanolamine (TEA) was added at increasing levels to B2 and C2 formulations are summarized in Table IV. Formulation B2 is 20% polyacrylic acid plus 80% methyl cellulose. Formulation C2 is 20% 1:1 copolymer of vinyl methyl ether and maleic anhydride, 80% methyl cellulose. Figures 3 and 4 correspond to the experiments with B2 and C2 respectively. The resistance decreases with increasing TEA in both cases. Substantial increases in flexibility were effected at amine levels above about six percent.

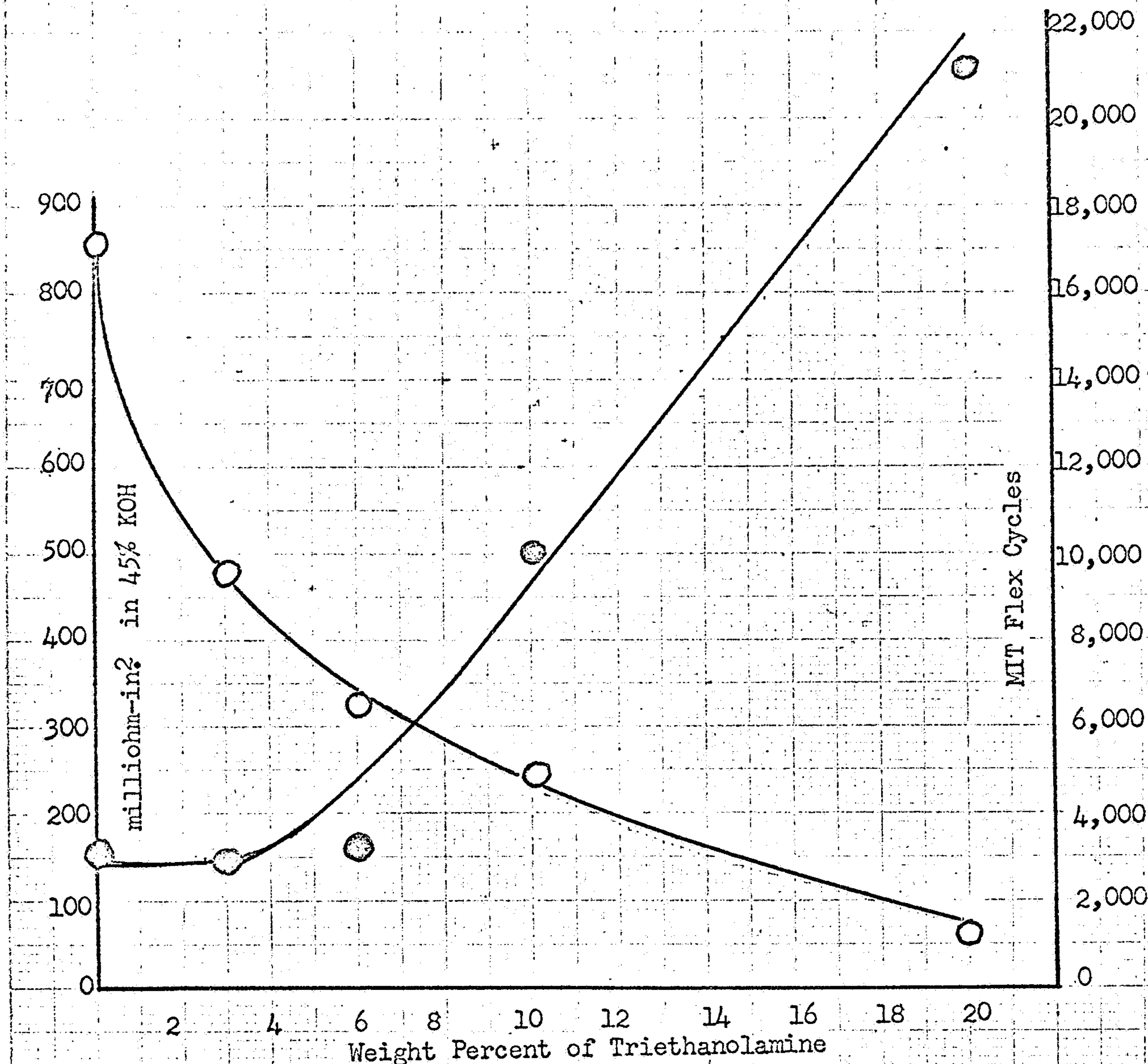


Fig. 3. Effect of Triethanolamine on Flex (◎) and Resistance (O) of B2 Films

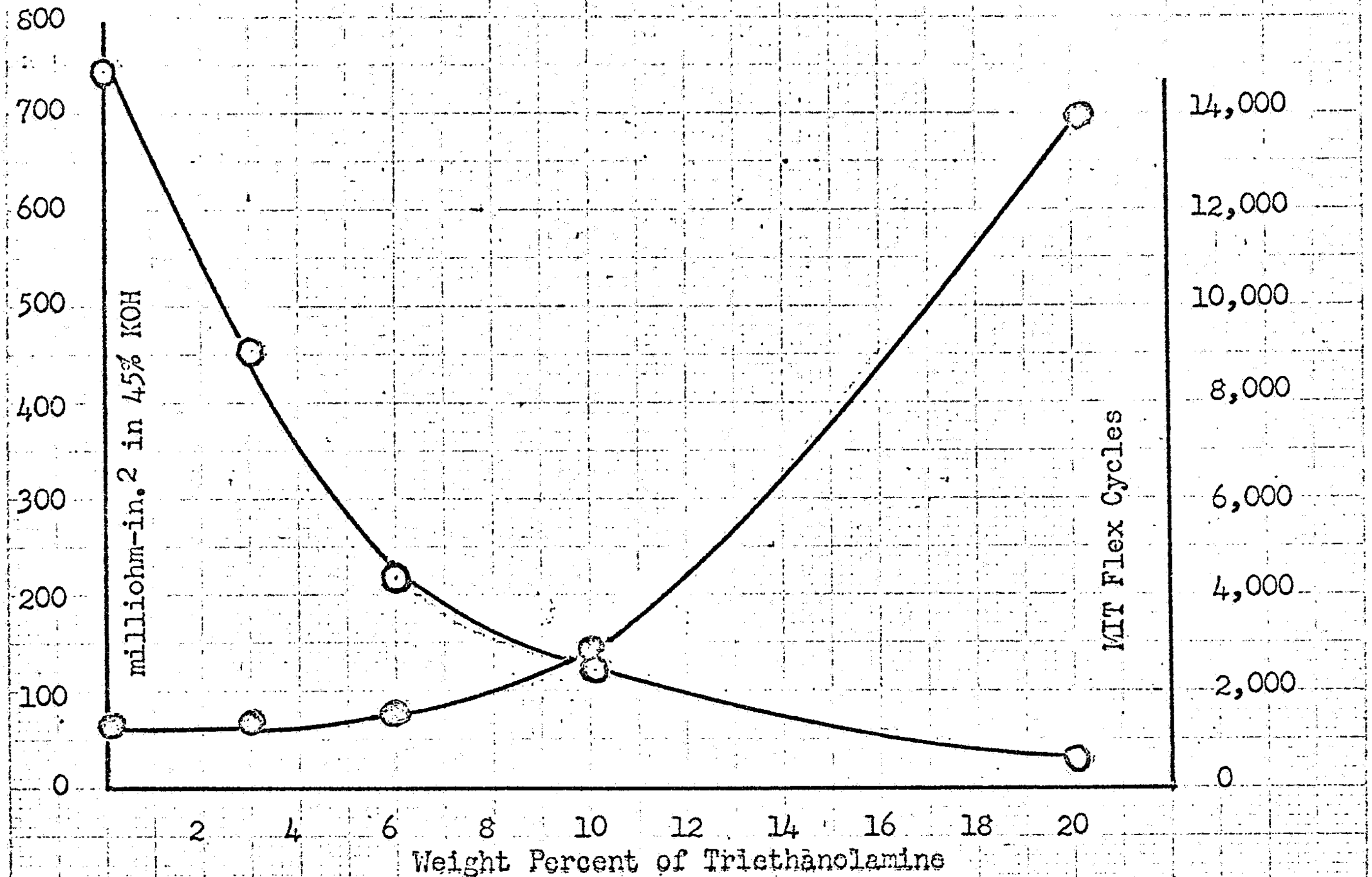


Fig. 4. Effect of Triethanolamine on Flex (●) and Resistance (○) of C2 Films

TABLE IV. - Films Modified with Triethanolamine

Reference	Polymer Formulation (a)	TEA % on Polymers	pH (b)	Resistance in 45% KOH milli-ohms-in.^{2}	Physical Properties - 72° F. - 50% RH MIT Flex (c) mils	cycles	Tensile Strength (d) psi	Elong.%
522-22	B2	0	2.8	848	1.5	3,001	10,830	25
522-27	B2	3	3.9	477	1.3	2,815	10,700	6
522-28	B2	6	4.1	327	1.4	3,181	9,070	18
522-29	B2	10	4.5	245	1.3	9,850	7,000	20
522-30	B2	20	5.3	60	1.4	21,000	5,220	26
522-24	C2	0	2.8	738	1.5	1,239	12,600	8
522-31	C2	3	3.6	448	1.9	1,324	11,300	5
522-32	C2	6	3.8	216	1.4	1,623	10,070	6
522-33	C2	10	4.1	122	1.3	2,838	7,470	22
522-34	C2	20	5.7	29.1	1.4	13,850	4,870	27

(a) B2 is 20 parts by weight polyacrylic acid plus 80 parts methyl cellulose.

C2 is 20 parts by weight poly(vinyl methyl ether-maleic anhydride 1:1) and 80 parts methyl cellulose.

(b) pH of a 10% aqueous solution of polymer mixture after addition of stated amount of triethanolamine.

(c) ASTM Test D643-43, at 200 g. tension.

(d) 1 inch span 2 inches per minute.

The pH of the solution from which C3 film is customarily cast is 2.8. Calculation shows that this corresponds to sufficient acidity to lower the electrolyte concentration in a tightly packed cell from 30% to 25%. It was therefore pertinent to study the effects of KOH additions to the casting solution. Films cast from solutions buffered to pH 6 and pH 8 respectively were found to have resistances in 45% KOH of 33.8 and 18.8 milliohms-in.^{2} as compared to 503 milliohms-in.^{2} for customary unadjusted C3 at pH 2.8. The lowered resistances were accompanied by increased silver diffusion from 1.9% per day to 5.4% per day, expressed in arbitrary units of percent of the silver initially charged to one side of the membrane. (See p. 6 of Appendix I for definition of these arbitrary units.)

Films cast from buffered solutions had a disadvantageous tendency to fissure on drying. No drying method was found to prevent the fissuring tendency. The condition was corrected by including 5% on polymer of either tetraethyleneglycol or triethanolamine.

The following films containing organic bases and/or sufficient potassium hydroxide to buffer to pH 8 were tested in cells at Electric Storage Battery Co. Compositions are given in parts by weight.

NAS 5-9107-25	80 methyl cellulose 20 PVM/MA 10 hydroxypropylamine
NAS 5-9107-31	70 methyl cellulose 30 PVM/MA; KOH to pH 8; 5 triethanolamine
NAS 5-9107-32	70 methyl cellulose 30 PVM/MA; KOH to pH 8; 5 tetraethyleneglycol

Poor cycle life was encountered in the tests on these cells. This may have been related to the high rates of silver diffusion found for these films. Study of their performance in layered combination with silver-scavenging types might prove fruitful. In such application it would be desirable to study also the kinetics and equilibrium involved in the partition of extractable amines between the respective membranes and the electrolyte liquid.

C. Modification of Methyl Cellulose Films with Salts of Organic Acids

Continuing work initiated under the previous contract,[a] a large number of aliphatic organic salts were investigated as additives to methyl cellulose or methyl cellulose-polyacid compositions.

New results are summarized in Table V. The dependency of electrolytic resistance on the salt equivalents per methyl cellulose monomer unit is illustrated in Figure 5. It is evident that the lower members of the homologous series show a downward trend in resistance as the salt equivalent is increased. Within the precision limits of these experiments the dibasic salts follow nearly the same trend as the monobasic salts. Salts of the higher members of the aliphatic series beginning with valerate are poor in lowering resistance.

Several of these film compositions were more flexible than methyl cellulose itself. This is attributable to the hygroscopicity of the salts. Such an effect is particularly advantageous at low humidities.

Most of the salts of lower aliphatic acids are soluble in 30% KOH. Their partial extraction by electrolyte may therefore play a role in the observed lowering of electrolytic resistance. If films containing organic salts are immersed in a large excess of stirred 30% KOH, they do lose their salts completely. This was most elegantly shown in an experiment with a film containing potassium lactate enriched with a trace of radioactive sodium lactate (CalbioChem, Los Angeles). After stirring for a week in excess 30% KOH, the count/min. of the film was reduced from 52,000 to 58. Similar conclusions were reached on the basis of ash determinations of electrolyte-saturated, blotted films. It remains to be established how nearly complete the extraction actually is in the unstirred and low electrolyte ratio conditions of a battery cell.

The following methyl cellulose modifications with salts were tested as films in cells at E.S.B. Compositions are expressed in parts by weight.

NAS 5-9107-22	90 methyl cellulose, 10 PVM/MA/28 potassium lactate
NAS 5-9107-23	100 methyl cellulose, 33 potassium acetate
NAS 5-9107-24	100 methyl cellulose, 17 potassium acetate
NAS 5-9107-28	100 methyl cellulose, 32 potassium succinate

The tests on these cells, summarized in the tables and graphs on pages 8 to 11 of Appendix II, indicate that Number 23 showed good cycle life in 45% KOH and Number 22 performed well in 30% KOH. An additional advantage of the latter film is its high flexibility at low humidities.

(a) NAS 5-9107 Final Report

Table V. Modification of Methyl Cellulose with Potassium Salts of Organic Acids

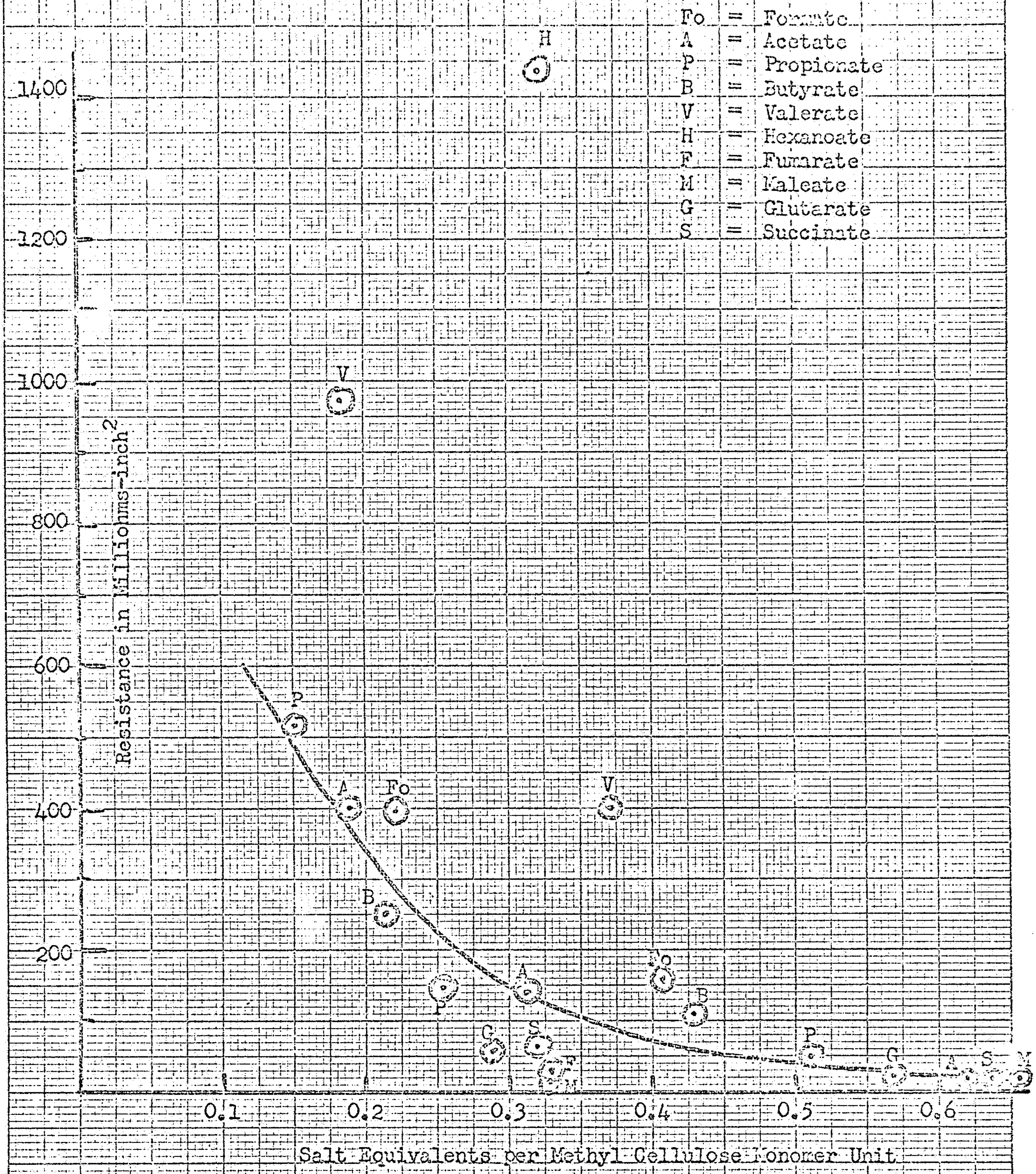
Reference	Potassium Salt Added	Weight % on MC	Weight % Equiv./ Equiv.MC	Elec.Res. 45% KOH milli-ohms-in.^{2}	Film Thick-ness mils	MIT Flex Cycles (X)	Tensile psi	Tensile Elong. %
Monobasic Acids								
449-145	None	0	0	7250	1.50	5,355		
534-56	Propionate	9.1	.152	515 (A)	1.45	5,234	8,040	47
-57	"	15.2	.254	147 (A)	1.8	5,015	6,290	51
-58	"	30.2	.510	50 (A)	1.9	12,230	3,500	57
534-91	Butyrate	14.3	.214	226 (A)	1.4	5,154	-	-
482-121	"	28.6	.428	110 (A)	1.4	7,591	-	-
534-130	Valerate	13.7	.184	971	1.4	4,190	5,640	47
534-129	" (F)	27.4	.372	400	1.5	6,917	6,790	32
534-132	Hexanoate	13.3	.162	2444	1.5	3,998	7,880	39
534-131	"	26.6	.324	1435	1.6	4,530	5,640	47
Dibasic Acids								
534-126	Glutarate	16.4	.29	57	1.5	3,154	6,260	45
-125	" (F)	32.9	.57	21	1.6	2,735	3,830	36
534-128	Succinate	15.8	.32	66	1.5	3,467	6,620	43
-127	" (F)	31.6	.64	20	1.6	1,508	4,000	34
482-140	Fumarate (F)	16.3	.33	32.9	1.8	3,514	6,760	40
-139	" (F)	32.6	.66	12.0	1.5	1,724	6,100	20
482-142	Maleate	16.3	.33	25.6	1.5	3,656	6,750	38
-141	"	32.6	.66	14.8	1.65	648	4,280	26

(A) Measurements in Shair cell, with less sensitive equipment than Kelley Salkind Cell now used.

(F) Frosted out on standing.

(X) ASTM Test D643-43, at 200 g. tension and 50% R.H.

Fig. 5. Dependence of Film Resistance Upon Equivalency



D. Modification of Straight Methyl Cellulose Films with Bases

The use of inorganic and organic bases to enhance the conductivity of methyl cellulose was described in the Final Report of previous Contract, pp. 7-10. The investigation was extended under the present Contract to include the quaternary ammonium bases, tetramethyl and tetraethyl ammonium hydroxide. These showed to advantage over formulations earlier reported, giving lower resistance as well as good flexibility.

Properties of the films are summarized in Table VI in comparison with a typical C3 film, with previous formulations with higher molecular weight quaternary ammonium hydroxides, and with a formulation with KOH.

Table VI. - Formulations of Methyl Cellulose with Hydroxide Bases

Reference	Base	Base % on MC	Elec. Resist. ohms-cm 30% KOH	Elec. Resist. ohms-cm 45% KOH	MIT Flex 50% R.H. Cycles	Tensile 50% R.H. psi	Thickness Dry mils
545-64	Me_4NOH	10	29.2	46.7	5,295	6,640	1.5
545-20	Et_4NOH	10	46.8	278.	-	-	1.5
545-21	Et_4NOH	20	15.2	69.	-	-	1.5
504-139	$BzMe_3NOH$	10	-	1,820.	4,745	-	1.5
522-62	KOH	9	55.	66.9	7,926	4,780	1.5
499-15 C-3	-	-	16.0	503.	754	14,700	1.5

Notes: Me = Methyl; Et = Ethyl; Bz = Benzyl; C3 = 30% PVM/MA, 70% methyl cellulose

Two compositions were tested in cells at Electric Storage Battery Company. They were the following, compositions being given in parts by weight:

NAS 5-9107-27 100 methyl cellulose, 10 tetramethyl ammonium hydroxide
NAS 5-9107-21 100 methyl cellulose, 9 potassium hydroxide

Both of these cells showed superior performance in the E.S.B. tests, as shown in Appendix II, particularly in the tables and graphs on pages 8 to 11.

The methyl cellulose-tetramethyl ammonium hydroxide separator was selected as one to be used in preparing the cells called for by Contract. It was prepared at 1.5 mils thickness for conventional U wraps and at 0.75 mils thickness to be used in conjunction with a 0.75 mil separator, NAS 5-9107-29 (polyvinyl alcohol 42-88) in wrapping with a double U wrap.

E. Modification of Methyl Cellulose and Methyl Cellulose Compositions by Pre-Swelling in 15% Potassium Hydroxide

The resistance of methyl cellulose films in 30% and 45% KOH can be greatly reduced by pre-soaking in 15% KOH. The initial swelling is maintained in the higher concentrations. This property is accompanied by increased silver diffusion rate.

When methyl cellulose film, after pre-swelling in 15%, was equilibrated by three days stirring in a large excess of 30% KOH, the following results were obtained:

	Pre-Swollen in 15% KOH then Equilibrated in 30%	Directly in 30% KOH
Swollen wt./orig.wt.	1.25	1.485
Resistance in 30% KOH milliohms-in.^{2}	17.3	498
Silver diffusion rate, in arbitrary transfer units defined on Page 6 of Appendix I.	8.2	0.24

These results indicate that the pre-swelling in 15% KOH opened the membrane up not only to hydrolysis but to silver ions as well. It is therefore likely that membranes pre-treated in this manner may be more useful in systems combining them with adequate layers of silver-scavenging membranes. There may also be uses for the pre-swollen films alone in cells other than silver-zinc.

The pre-swelling procedure was extended to include compositions with polar additives, including respectively polyacids and potassium acetate. As shown in Table VII, resistances were lowered still further by the combination of polar addition and pre-swelling. In some cases the resistances were below those of swollen cellophane. For example, the B3.3 film had a resistance of 2.8 ohms-cm. in 30%, 4.5 ohms-cm. in 45% KOH, the latter figure being one-hundredth of the value obtained on B3.3 film equilibrated directly in 45% KOH. It is probable that silver diffusion rate would also be greatly increased.

A practical method of exploiting this property of methyl cellulose compositions would be to wrap electrodes with the separator, condition first in 15% KOH, then equilibrate the assemblies in the electrolyte of the concentration employed in the cell.

It is recommended that further study be given to this pre-swelling technique and the pre-swelling treatment discussed in the following section F. Representative pre-swollen films should be tested in cells.

TABLE VII.- Effect of Pre-Swelling Films in 15% KOH on Resistance in 30% and 45% KOH

	MC 485-118	C1 421-116	C2 421-102	B2 522-105	B3.3 504-29	MC + 33% KOAc 534-63
Dry Thickness - mils	1.5	1.5	1.5	1.5	1.5	1.5
Swollen Thickness - mils						
Directly in 30% KOH	1.88	2.10	2.13	2.3	2.3	1.8
15% → 30% KOH	2.44	2.0	2.3	2.6	2.8	3.1
Resistance - ohms-cm						
Directly in 30% KOH	498.	71.2	22.6	152.	26.5	28.1
15% → 30% KOH	17.3	10.3	9.1	6.7	2.9	4.8
Dry Thickness - mils	1.5	1.5	1.5	1.5	1.5	1.5
Swollen Thickness - mils						
Directly in 45% KOH	1.83	2.07	2.28	1.9	2.1	1.74
15% → 45% KOH	2.52	2.30	2.20	2.8	2.8	3.1
Resistance - ohms-cm						
Directly in 45% KOH	6080.	905.	738.	635.	574.	53.8
15% → 45% KOH	60.	11.2	7.4	9.5	4.5	5.6

NOTES:

MC	Methyl Cellulose	
C1	10% PVMMA/90% MC	
C2	20% PVMMA/80% MC	
B2	20% PAA/80% MC	+ KOH to pH 5
B3.3	33% PAA/67% MC	+ KOH to pH 4

F. Modification of Methyl Cellulose and Methyl Cellulose Compositions by Pre-Cooling in Electrolyte

Cooling a methyl cellulose film in 30% KOH at just short of the freezing point (-58° C.) followed by re-equilibrating at room temperature increases conductivity about 10-fold. This is accompanied by increased swelling and increased permeability to silver. The increased conductivity level showed no change over a 4-month period.

In using the same technique (-58° C. in 30% KOH) on a B3.3 film (67% methyl cellulose; 33% polyacrylic acid) resistance was reduced from 26.4 ohms-cm to 6.5 ohms-cm, about that of cellophane.

When a film of methyl cellulose containing only 0.5% KOH was treated at -58° C. in 30% KOH, the film was swollen to ten-times its original thickness.

The concentration of the KOH in which the film is pre-cooled is a factor in determining the degree of swelling. Thus, while the above mentioned four-fold increase in the conductivity of B3.3 film was attained by pre-cooling in 30% KOH, the corresponding use of 45% KOH brought about only a slight increase in conductivity. Time was not available to study in complete detail the effect of KOH concentration in the case of straight methyl cellulose. As shown in the preceding section, a swelling action is achieved by using lower concentrations of KOH even at room temperature.

It is recommended that further study be given to the preparation of this pre-swelling technique and the pre-swelling treatment discussed in the proceding section E. Representative pre-swollen films should be tested in cells.

A practical method of applying the pre-cooling principle in battery cells would be to assemble the cells as usual with dry membranes, then add electrolyte and cool the entire cell in a cold box.

The fact that the properties of methyl cellulose type films are affected by exposure to cold alkali must be kept in mind in their application in battery cells. For example, in space applications temperature control should be adequate to maintain all film properties including electrolyte resistance within desirable limits.

G. Wrapping Electrodes with Separators

In the conventional U-wrapping technique two silver electrodes are placed butt ends opposing across the lateral dimension of a rectangular separator strip and folded for several wraps (usually 5 or 6) in the longitudinal direction. The assembly is then folded at the median line to give a U-bend enclosing the electrodes. This manipulation results in tension at the bend, and, in some cases, development of cracks, especially in the outer fold.

An effective means of relieving the stresses at the bond was found to be the application of a plasticizing solvent at the median line before bending. Electrolyte solution itself is a particularly appropriate plasticizing material since it swells the film without dissolving it.

Flexibility as measured by the MIT folding test is not always correlated with U-bend stress. Separator NAS 5-9107-22, for example, has a high MIT flex (7926 cycles, while NAS 5-9107-21 has a lower flex (1920 cycles). Yet the -22 film has been found to have a greater tendency to crack at the U-bend than -21 film. This was the case in wrapping tests under controlled humidity at Borden. It was also found that -22 film in cells prepared at Burgess had numerous cracks at the U-bend, whereas -21 film in Burgess cells showed no cracks.

H. Envelope Separators

The use of envelopes around the zinc electrode is of interest because sluffed-off electrode material would be confined near the electrode instead of settling at the bottom of the cell. An exaggerated class of zinc electrode dislodgment is encountered in the use of an experimental "pressure cell" described on page 12 of the appended E.S.B. report. In this cell with conventionally wrapped C3 film, it was not possible to exceed six cycles. Several experiments were therefore run with envelopes confining the zinc electrode.

The envelopes for these experiments are listed at the bottom of Table I on page 6 and the E.S.B. tests are reported on pp. 13 and 14 of Appendix II. The envelopes were constructed at Borden Chemical Company by folding the substrate sheet around a polyethylene electrode templet, then sealing the side edges. One type used Viskon S250CM paper as substrate and polyvinyl acetate as sealant. Envelopes 545-65 and 563-46 were dip-coated with polyvinyl alcohol 42-88; envelope 563-47 was dip-coated first with the polyvinyl alcohol, then with a composition corresponding to that of C3 film. Envelope 563-56 was constructed by heat-sealing a polyvinyl alcohol-C3 laminate film without paper substrate. Cycle tests with the envelopes showed a significant improvement over the use of C3 alone. One out of two runs with 563-56 lasted 7 cycles. Two out of three runs with the 545-65/563-46 type lasted through the entire ten cycles of the screening. One out of two runs with 563-47 also lasted ten cycles. These results cannot be considered definitive, however, since several parameters have been confounded, including total separator thickness, pressure on the assembly, electrolyte-electrode ratio, nature and geometry of sealant and seal, as well as chemical identity of the separators. If future work should be undertaken to evaluate envelopes vs. conventional wrapping procedures, tests should be statistically designed to evaluate the effects of the several parameters.

J. Irradiation of Cells Constructed with C3 Film

C3 film recovered from a battery cell exposed to irradiation by Cobalt 60 still had 76% of its initial wet tensile strength. Cellophane likewise exposed had its layers welded together.

Two sealed silver-cadmium cells (Yardney) with C3 separators were received from NASA for examination. One had been irradiated with 1.18×10^7 rads from a Cobalt-60 source. The other had been kept as a control in an oven, without radiation, at temperatures between 40° and 55° C. during the time of the irradiation test. A corresponding two cells with cellophane separators instead of C3 were likewise used for irradiation and control in the NASA test and returned to Yardney for examination. NASA reports that the layers of cellophane in the irradiated cell were very tightly "welded" together and tore when attempt was made to separate them, so that strength could not be determined.

Both polystyrene cell-case and potting of the irradiated cell were discolored to brown. The control cell appeared relatively unharmed. The cells were carefully opened with the aid of a fine saw. The electrolyte was removed from each cell and the C3 membranes were unwrapped, cut into strips for tensile tests and stored in 30% KOH until tested.

The films from both cells were visibly silvered. Their thickness was less than the expected swollen thickness. The 436-134 lot of C3 film from which Yardney prepared the cells had average thickness 1.5 mils, which swells in 30% KOH to 2.2 mils. Yet the irradiated and control cells yielded material of thickness 1.6 and 1.4 respectively. It is not clear to what extent the discrepancy is attributable respectively to film erosion. or to reduced swelling in the geometrical confines of the shim-modified cell.

Tensile tests are recorded in Table VIII. Inspection shows that elongation is significantly reduced by the irradiation to 4% instead of 26% for the control. Average tensile strength was reduced by irradiation from 1.59×10^3 psi to 1.22×10^3 psi ($\pm 0.20 \times 10^3$ psi, pooled standard deviation). Statistical analysis of variance, by F-test indicates less than 3% chance that this difference could be due to random variation.

TABLE VIII. - Effect of Irradiation on Tensile Properties of C3 Film

Wrap No. from Ag Electrode	Control (#19 Cell)				Irradiated (#7 Cell)			
	Thickness Avg. mils	Lbs. to Break	Tensile psi	Elong. at Break %	Thickness Avg. mils	Lbs. to Break	Tensile psi	Elong. at Break %
5	1.60	1.615	1637	32	1.43	1.315	1557	7
4	"	1.613	1703	33	"	.817	966	3
3	"	1.603	1697	32	"	1.078	1277	3
2	"	1.493	1493	15	"	1.075	1067	3
1	"	1.346	1430	19	"	Too weak to test		
Avg.	1.60	1.534	1592	26	1.43	1.071	1217	4

K. Gas Evolution in Charging Cells Made with C3 Film

NASA reported that frothing had been observed during the charging of certain cells made with C3 separator. These were 10-ampere hour Ag/Zn cells made by Burgess Battery Company. Several similar reports have also been received from other sources.

A battery of three cells of C3 was charged in the Borden laboratory and gas collected. This was shown to be neither oxygen nor CO_2 and may therefore be presumed to be hydrogen. Frothing during this period of overcharging was not sufficient for foam to escape from the cell.

C3 is known to be quite insoluble in 30% KOH. However, with the separator/electrolyte ratios of a tightly packed cell the acidity of the membrane would initially reduce the overall concentration of KOH to 25%. It is possible that trace amounts of surface active material could dissolve at this concentration and be responsible for the frothing. It was found impossible to induce serious frothing under simulated conditions.

It has been found that a trace of 1% solution of a silicone antifoam (Antifoam 10, General Electric) is very effective in reducing foam under simulated battery conditions of foam. It is not known how this addition would affect other aspects of battery performance.

I. Storage Under Charged Condition of Cells with C3 Film

The effect of standing in a charged condition was studied using 10-ampere-hour silver-zinc cells. These were SS 5.5 type cells constructed by Burgess Battery Company, Freeport, Illinois, using six silver plates and seven zinc oxide plates. The former were U-wrapped with five turns of C3 film. A battery of such cells was charged and discharged three times, with successive stand times in the charged condition of 76, 104 and 174 days on the same battery. After the respective periods of stand the ampere hour capacity of the three cells averaged 8.93, 7.08 and 2.53 A.H. respectively. This was considerably better behavior than the reported complete failure of silver-cadmium C3 cells at Jet Propulsion Laboratories. These were said to have shorted after a single stand time of three months.

Silver analysis of the disassembled wraps showed a gradient distribution of silver from the first to fifth wraps of 21.7 mg Ag/sq.in. to 2.05 mg Ag/sq.in. This was similar to the distribution found in a Ag/Zn-C3 cell after 85 cycles at NAD Crane.[a] The JPL cell showed a uniform distribution of around 8 mg. from wrap to wrap. The significance of this difference in distribution characteristics is not understood.

It is generally accepted that during stand in the charged condition shorting or loss in A.H. capacity results from slow diffusion of silver, setting up a "soft short" during long stand periods. If this is a valid explanation the use of alternate thin layers of oxidizable membranes which stop silver completely, with oxidation resistant membranes, which permit small quantities of silver diffusion, might be expected to remedy the stand time problem.

(a) T. J. Hennigan, Separator Materials for Silver Oxide Zinc and Silver Oxide Cadmium Electrochemical Cells, Goddard Space Flight Center, X-716-65-331 (1965).

M. Non-Cellulosic Separators

Synthetic membranes of copolymers of methacrylate ester and acrylic acid were prepared by solution polymerization in which the molar proportion of acrylic acid was such as to give conductivities in the useful range in 45% KOH. These membranes, like the methyl cellulose compositions, were water-soluble but insoluble in the electrolyte. The molar proportion of acrylic acid in the copolymers was in the range of 40 to 50%.

The solution polymers were brittle in the acid form but gave fairly flexible films when partially neutralized with inorganic or organic bases. Resistance to oxidation by silver oxide was excellent. Because silver diffusion rate was correspondingly high, exploitation of these films is more likely to be of interest in layered combination with silver-scavenging films.

A 34 mol per cent copolymer of acrylic acid with methyl methacrylate; prepared by emulsion polymerization, was water insoluble but was of too high resistance to be of interest.

A second type of non-cellulosic membrane was based on co-acervated films prepared by casting homogeneous aqueous solutions of polyvinyl pyridine hydrochlorides and polyacids and evaporating the cast films until free of chloride. One such separator, a co-acervate of molar equivalents of poly-4-vinyl pyridine and polyacrylic acid had a resistance of 8.7 ohms-cm in 30% but also a correspondingly high silver ion diffusion rate. The film was highly resistant to oxidation. It showed a remarkable stability to heating in 30% KOH and 45% KOH at 50° C. After 33 days it was still intact in both solutions. Resistance was slightly lowered after the heating period.

These films are water-insoluble, but highly swollen by concentrated alkali. Tensile strength was 2950 psi. MIT flex was quite low at 90 cycles. In the present state of their development these films have several deficiencies which might be corrected by further research. In addition to the brittleness in the dry state they are weak in the swollen state.

A third class of non-cellulosic membranes was based on polyethylene. Films made respectively from polyethylene and from Surlyn A1601, a du Pont modification of polyethylene, were soaked in solvents under such conditions as to give observable swelling short of solution. The swollen films were then extracted with a second liquid in which the swelling solvent was soluble or which reacted with the swelling solvent. One such system used phosphorus trichloride as solvent, and water and potassium hydroxide as solvent-reactant for the phosphorus trichloride. Resistance in 45% KOH was lowered as much as three orders of magnitude but was still too high to be of practical interest (2.9×10^3 milliohms-in.^{2}).

N. Silver Ion Diffusion Through Separator Membranes

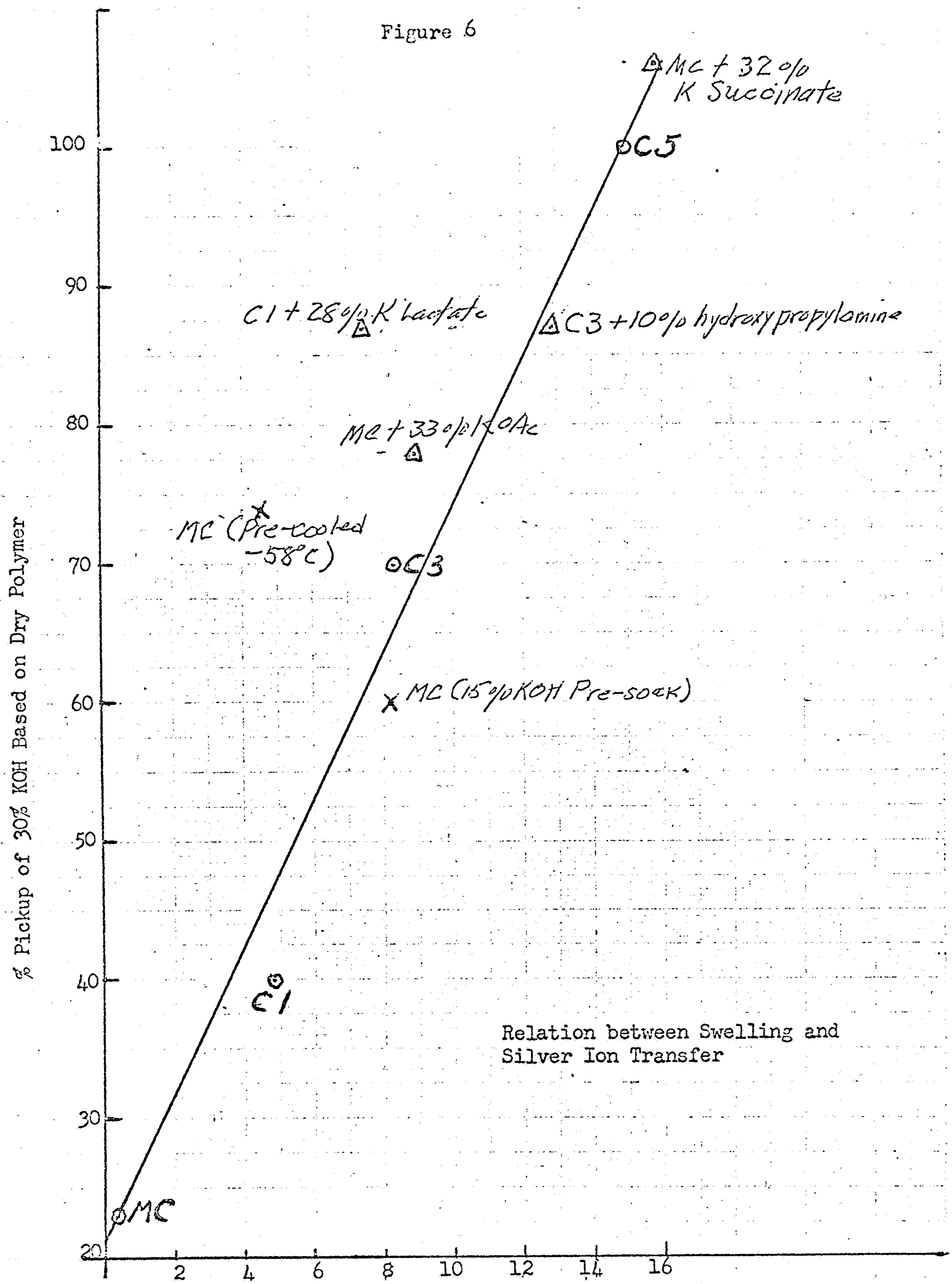
The diffusion of silver ions through the membranes of this project was studied by a radioactive tracer technique. The entire Second Quarterly Report was devoted to this subject and is reproduced in full as Appendix I of this final report. It was concluded that membranes which restrict the passage of silver ions from solution of silver oxide in potassium hydroxide fall into two broad classifications. Oxidizable films are initially very effective barriers to silver ions by reducing them to metallic silver, but it is known from earlier work that the oxidative degradation of the membrane may lead to eventual catastrophic damage. Non-oxidizable membranes which retard silver ion diffusion tend to retard also all electrolytes. Therefore electrolytic resistances are higher when silver diffusion rates are lower.

Based on these observations, it appeared pertinent to compare in extended tests in cells the relative merits of superior examples of the oxidizable and non-oxidizable types, alone and in combination. Hence the selection for the cells to be provided under this Contract included an oxidizable polyvinyl alcohol film, a non-oxidizable film compounded from methyl cellulose and tetramethyl ammonium hydroxide, and a combination of thin films of both these materials.

The experiments on silver diffusion included a series using as electrolyte 30% potassium hydroxide saturated with zinc oxide. A variety of membrane types showed the same behavior toward silver ion as when the solution contained no zinc oxide.

Data presented in Appendix I indicate also a rough correlation between the rate of silver transfer through a film and the degree of swelling in the electrolyte. Apparent exceptions to the correlation were films comprising methyl cellulose and low molecular weight components such as salts and amines. However, the degree of swelling used was calculated on the basis of the weight increase over dry film. Since the swelling tests were made with sufficient excess of electrolyte solution to remove all the components of low molecular weight it is proper to apply a swelling factor based on the polymeric components of the film alone. When this is done, the several films containing salts or amines follow the same correlation between swelling and silver transfer which holds for C-type films. This is illustrated in Figure 6. Methyl cellulose pre-swollen in dilute potassium hydroxide also falls close to the line. Methyl cellulose pre-swollen by cooling deviates somewhat more from the line, indicating that the two types of swelling may not lead to exactly identical products.

Figure 6



Arbitrary Silver Ion Transfer Factor
(% Ag/da in Experimental Cell)
as defined on p. 6 of Appendix I.

ITEMS OF NEW TECHNOLOGY

In the preceding Contract, NAS 5-9107, items A, B, C, D, E, F, G, H, and J were disclosed. Inasmuch as the present Contract is known as Modification 6 of the same number NAS 5-9107, the new items herewith disclosed are designated as K, L, M, N, P, Q, R, S, T and U, to avoid confusion between the two sets of items. Cross references to related disclosures have been made.

K. METHYL CELLULOSE-POLYACID FILMS MODIFIED WITH BASE

Methyl cellulose-polyacid films may be prepared with low resistance in 45% KOH by casting from solutions buffered to pH between 3 and 8. At pH above 4 hydroxyamines like 3-hydroxypropylamine and triethanolamine are more effective than potassium hydroxide in that they act as flexibilizing agents for the dry film, making for superior facility in handling.

Addition of 10% triethanolamine to B2 formulation (20% polyacrylic acid; 80% methyl cellulose) lowers resistance by 70%, increases flexibility by 33%. Addition of 10% triethanolamine to C2 formulation (20% 1:1 copolymer of vinyl methyl ether and maleic anhydride; 80% methyl cellulose) lowers resistance by 83%, increases flexibility by 230%.

Both hydroxypropylamine and triethanolamine are completely soluble in 45% KOH and have been shown to be extractable under conditions of the resistance test. The extractability is believed to be a factor in the lowered resistance.

When the pH of this type of film is higher than 6, it becomes difficult to prepare uniform films. Further development work would be necessary to establish manufacture on a practical basis.

References: This Final Report, pp. 8-16, 20
Third Quarterly Report, p. 10
First Quarterly Report, pp. 4-11
See also Final Report NAS 5-9107, pp. 4-10

L. METHYL CELLULOSE FILMS MODIFIED WITH SALTS OF ORGANIC ACIDS

In extending the study of this type of system to include higher aliphatic acids and lower dibasic acids, resistance lowering was found to be related to the acid equivalents per methyl cellulose monomer unit.

References: This is a continuation of Item E; see
Final Report NAS 5-9107 pp. 13-16; Conclusion 5
This Final Report, pp. 17-19
First Quarterly Report NAS 5-9107 Mod. 6, pp. 12-14, 18

M. IMPROVING CONDUCTIVITY OF METHYL CELLULOSE COMPOSITIONS BY PRE-SWELLING IN 15% POTASSIUM HYDROXIDE

Pre-soaking methyl cellulose membranes in 15% KOH not only lowers their electrolytic resistance in either 30 or 45% KOH, but also increases swelling and permeation to silver ion. Application of the pre-soaking procedure to compositions in which methyl cellulose is modified by polar additives can result in still greater changes. Electrolytic resistance can be decreased to levels lower than that of cellophane. Since silver diffusion rates would be correspondingly high, such films by themselves might not be appropriate for secondary Ag/Zn or Ag/Cd cells. Study of their use in layered combinations with films which scavange silver is recommended. Investigation in other types of cells, such as zinc-oxygen is also recommended.

References: This is a continuation of Item E; see
Final Report NAS 5-9107 pp. 11, 12
First Quarterly Report NAS 5-9107 Mod. 6 p. 15
Third Quarterly Report NAS 5-9107 Mod. 6 pp. 7,8
This Final Report pp. 21-22

N. PRE-COOLING MEMBRANES IN CONCENTRATED ALKALI TO INCREASE THEIR CONDUCTIVITY

Pre-cooling a methyl cellulose membrane at below -55° C. in 30% KOH lowered the resistance of the membrane at room temperature from 590 to 60 milliohms-in.^{2} The low resistance persisted over a 134 day period. Increased swelling and increased diffusion rate for silver were also brought about.

Application of a similar pre-cooling cycle to compositions of methyl cellulose modified by polar additives can result in still greater decreases in resistance, even to levels lower than that of cellophane. Since silver diffusion rate would be correspondingly high, such films by themselves might not be appropriate for use in secondary Ag/Zn or Ag/Cd cells. Study of their use in layered combinations with films which scavenge silver is recommended. Investigation in other types of cells, such as zinc-oxygen is also recommended.

References: Third Quarterly Report NAS 5-9107 Mod. 6 pp. 4-6
This Final Report p. 23

P. SEPARATOR FILMS FROM METHACRYLATE-ACRYLATE COPOLYMERS

Films may be made from certain co-polymers of methacrylate esters with acrylic acid. When partially or completely neutralized with inorganic or organic bases, films were obtained which were sufficiently flexible to be handled in operations such as wrapping electrodes. The films were oxidation-resistant and in some cases gave resistance values as low as cellophane. At such levels, however, permeability to silver was relatively high. The co-polymers are prepared by selective hydrolysis of methacrylate ester with acrylate ester copolymers.

References: Third Quarterly Report NAS 5-9107 Mod. 6 p. 11, 12
(Item of New Technology V)
This Final Report p. 30
See also Final Report NAS 5-9107 p. 20

Q. PREPARATION OF NON-CRACKING U-WRAPS FOR ALKALINE BATTERIES

When the U-bend technique is used to wrap separator membranes around electrodes, it has been observed that even relatively flexible films exhibit a tendency to crack at the U-bend if not handled with excessive care. An effective way of decreasing the chance of such damage has been found to be the prior application of electrolyte solution to the area to be stressed. Other plasticizing solutions served the same purpose, but electrolyte solution has the advantage of substantially adding nothing to the final assembly.

References: This Final Report, p. 24
Third Quarterly Report NAS 5-9107 Mod. 6 pp. 20-22

R. POLYVINYL PYRIDINE-POLYACID CO-ACERVATE FILMS

A co-acervate of poly(4-vinyl pyridine) and polyacrylic acid may be prepared as a clear film by mixing aqueous solutions of the polyacid and the hydrochloride of the polyvinyl pyridine, casting the aqueous solution on glass and drying until chloride-free. The dried film is quite brittle but may be handled in flexible condition after soaking in electrolyte solution. The swollen film has relatively low resistance to electrolytic current, fair retardation of silver ion diffusion and very low vulnerability to chemical oxidation by silver oxide.

References: First Quarterly Report NAS 5-9107 Mod. 6 pp. 25, 26
Final Report NAS 5-9107 Mod. 6 p. 30

S. METHYL CELLULOSE-POLYACID FILMS MODIFIED WITH GLYCOLS

Ethylene glycol, diethylene, tetraethylene glycol and methyl cellosolve are all compatible with methyl cellulose and methyl cellulose-polyacid solutions and good films may be cast from these solutions. However, the glycols are not as effective as certain amines (Item K) in lowering the electrolytic resistance of the films in KOH.

References: First Quarterly Report NAS 5-9107 Mod. 6 pp. 15, 16

T. RESISTANCE OF METHYL CELLULOSE-POLYACID SEPARATOR TO IRRADIATION

A C3 separator recovered from a silver/zinc cell irradiated by Cobalt 60 had lost only 24% of its wet tensile strength. Composition of C3 is 30% 1:1 copolymer of vinyl methyl ether and maleic anhydride; 70% methyl cellulose. NASA reports that cellophane separators under the same exposure were welded together.

References: This Final Report pp. 26, 27
First Quarterly Report NAS 5-9107 Mod. 6 pp. 19,20

U. PROCEDURE FOR DETECTION OF IMPERFECTIONS IN MEMBRANES

A convenient method for detecting cracks or pinholes in a membrane is based on a test used in the paper industry for studying pinholes in paper (Grease Resistance Test ASTM D722, or TAPPI T454 ts-66).

A solution of a dye is prepared in a liquid which is a good solvent for the dye but a non-solvent for the membrane. In the case of most of the membranes of this project, hexane is a suitable solvent, using Du Pont Oil Red Powder as the dye. One gram of dyestuff is added to 100 ml of pure hexane, the stoppered bottle is shaken well and allowed to stand overnight. The solution is filtered through dry filter paper and stored in an airtight bottle.

The membrane is placed on a sheet of absorbent filter paper or chromatograph paper. The membrane is covered with an approximately quarter inch layer of 30-mesh Ottawa sand. Dye solution is then poured on to the sand in quantity sufficient to wet well. The assembly is covered with a glass dish or other convenient cover to inhibit evaporation. After 30 minutes the filter paper is examined for dye seepage.

This test is non-destructive and can be used to ensure that membrane envelopes have been properly sealed. The membranes may be recovered by removal of sand and dye, rinsing with hexane and air-drying.

APPENDIX I.

SILVER ION DIFFUSION

THROUGH

SEPARATOR MEMBRANES

TABLE OF CONTENTS

TABLE OF CONTENTS (CONTINUED)

INTRODUCTION

In the development of membranes suitable for exploitation as separators in silver-zinc and related types of battery cells, it is important to know how the membranes behave in contact with silver oxide dissolved in concentrated alkali. The present report describes the silver-barrier properties of a selection of membranes representing the chemical types which appeared most promising for consideration as improved separators. The radioactive tracer technique was essentially the same as described in the First and Final Reports of the previous Contract NAS-5-9107 (1964-5). The electrolyte medium used in the earlier studies was 30% potassium hydroxide saturated with silver oxide. The work herewith reported includes further tests with 30% potassium hydroxide saturated with silver oxide, tests with 45% potassium hydroxide saturated with silver oxide and tests with 30% potassium hydroxide saturated with both silver oxide and zinc oxide.

SUMMARY AND CONCLUSIONS

1. Membranes which restrict the passage of silver ions from solutions of silver oxide in concentrated potassium hydroxide fall into two broad classifications:

(a) One type of membrane initially halts passage of dissolved silver oxide by reducing it to metallic silver which precipitates out on the membrane. Functioning as reducing agent, the membrane becomes optimized. The resulting chemical and physical damage to the membrane eventually becomes sufficiently severe to destroy the function as separator.

(b) The other type of membrane acts chiefly by limiting the rate of silver ion diffusion. The conditions of chemical and physical structure which retard the passage of silver ions also tend to retard the passage of ions in general. Therefore electrolytic resistance tends to be higher when silver diffusion rates are lower.

2. Since no single membrane was encountered which oxidized all the desired properties, namely chemical inertness, low silver diffusion rate and low electrolytic resistance, it is pertinent to try combinations of the two types of membrane in separator systems. Also studied were two membranes which comprised polyvinyl alcohol in conjunction with methyl cellulose modifications.

3. At the 30% level of potassium hydroxide, a variety of membrane types showed the same behavior toward silver ion both when the electrolyte was saturated with zinc oxide and when it contained no zinc at all.

4. It has been demonstrated both by experiment and by mathematical proof that the rate of radioactive silver ion transfer through a non-oxidizable membrane has identical dependence on the initial concentration of radioactivity in the charged half-cell, regardless of whether the opposite half-cell initially contains no silver ion or is saturated with untagged silver ion.

EXPERIMENTAL PROCEDURE

The radioactive tracer procedure employed an apparatus based on Dirkse (1) and Weiss et al. (2). Concentrated alkali solutions were saturated with silver ions enriched with radioactive Ag 110 and silver transfer was followed by radioactive count.

The diffusion cell is illustrated in Figure 1. The half-cells are standard commercial pyrex ells. Using glass instead of methyl methacrylate has the advantage of minimizing silver losses through reaction with cell walls. As further precautions against extraneous silver loss, the gaskets on both sides of the tested film were made of polyethylene and the neoprene stoppers were not allowed to contact the silver solution.

The ells have internal diameter equal to one inch and are about four inches high and three inches across, conveniently accommodating 45 ml. of solution. The neoprene stoppers were fitted with capillary tubes to permit equalizing pressure.

The radioactive solutions were prepared by either of two alternative methods. According to one method, the appropriately concentrated potassium hydroxide solution was treated with silver nitrate solution enriched with radioactive silver 110 nitrate. The amount of silver nitrate was just in excess of that necessary to saturate the solution with silver oxide.

According to the alternative procedure, about one liter of appropriately concentrated KOH solution was saturated by stirring with excess silver oxide for several days, using a closed brown bottle and magnetic stirrer. The saturated solution was filtered through a fine sintered glass funnel into a brown glass bottle. Both funnel and receiving bottle had been cleaned with hot nitric acid and thoroughly washed with deionized water. Apparatus was protected from light throughout. An appropriate amount of radioactive silver 110 nitrate, nominally 100 microcuries, was dissolved in 2 ml. of the appropriate KOH solution containing no silver. This was then added dropwise to the silver oxide-saturated KOH solution with rapid stirring. Stirring was continued overnight. The solution was again filtered and stored in a clean brown glass bottle.

Circular disks, 1.5 inches in diameter were cut from the membranes to be tested. These were pre-soaked for at least three days in a large excess of the appropriately concentrated potassium hydroxide (either 30% or 45% by weight). Before insertion into the diffusion cell, each membrane was blotted free of supernatant liquid.

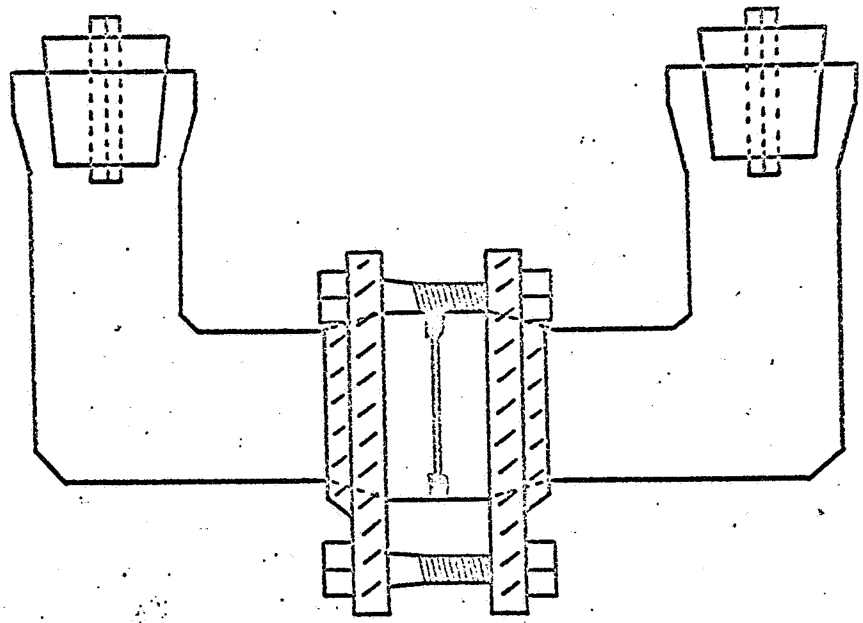


Figure 1

In each experiment the clean dry cell was assembled with membrane and gaskets inserted between the two sides. The sides were clamped together with the aluminum or iron flanges which are supplied with the commercial ells. In fastening the apparatus to its stand, care was taken to have it level. This was facilitated by a sight line on the wall behind.

The respective 45 ml. solutions were poured into the two sides either simultaneously or in quick succession. In the present report Side 1 denotes the side to which the originally radioactive solution was introduced. In most of the experiments here considered the solution introduced on Side 2 was the appropriately concentrated KOH solution without any silver oxide. This differs from earlier experiments in which the originally non-radioactive side was saturated with non-radioactive silver oxide. * The apparatus was shielded from light during the standing times by covering with a black cloth.

After recorded intervals of time, replicate 0.1 ml. aliquots were removed from each side of the diffusion cell and transferred to stainless steel planchets. Sampling was carried out with the help of fine microfilter tube-type pyrex fritted funnels (Fisher Scientific 20-700) accommodated with rubber stoppers to fit the cell openings. With the exception of the zero-time samples, each sampling was preceded by magnetically stirring the liquid in the two sides for one minute, using half-inch Teflon-covered bars.

Prior to transfer of sample, the planchets were outfitted with lens paper insets to assure uniform spreading of liquid. After equilibration, radioactivity was measured with a conventional scaler and flow counter. Ten one-minute counts were taken on at least two samples and averaged. Values were corrected for background noise. The radioactive count was converted to mg. Ag_2O per the 45 ml. charged using the Amlie and Ruetschi (3) values for saturation solubility (57 mg./l. in 30% KOH; 1.94 mg./l. in 45% KOH).

After sampling, the excess electrolyte was drained back into the half-cells. The loss due to retention in the microfilter is estimated at 0.3 ml. after each drainage.

At the conclusion of the diffusion tests, after sampling for terminal concentration values the cell was disassembled, the membrane rinsed in non-radioactive KOH of the concentration under test, blotted, and transferred to a tared 10 ml. volumetric flask. About 7 ml. concentrated nitric acid was added and the membrane was digested by warming on a hot plate. The cooled flask was weighed. One tenth ml. aliquots (.142 grams) were transferred to planchets which were dried under infra-red and counted. The count was converted to total silver oxide on membrane by multiplying by the pertinent factors.

Apparatus and pipettes were cleaned between tests by washing well with nitric acid followed by deionized water. When not sampling the apparatus was kept covered with dark cloths.

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* The two methods give comparable results. See pp. 8 to 10.

In spite of the care to avoid exposure to light, precipitated silver was observed in the diffusion cell liquid during some experiments. By withdrawing all samples through fine sintered glass microfilters, the presence of suspended or colloidal silver in the counted samples was avoided. No attempt was made to correct for the loss of radioactivity in solution during the course of an experiment by such occasional colloidal precipitation. Occasional irregular counts for which no satisfactory explanation could be given were excluded from the collated data.

In converting radioactive count to milligrams of Ag_2O, no corrections were made for sampling losses (up to 3%), for radioactive decay (less than 1.5%) or for loss to the vessel walls (less than 1%). In view of these facts, it is not surprising that the final accounting of radioactivity at the end of an experiment deviated considerably from the amount initially charged. The magnitude of this deviation is indicated in the column headed "Acc'd. for, % of original" in Tables VI, VII and VIII. On the average, based on sixty-three experiments, the summation of the weight remaining on Side 1, diffused to Side 2 and deposited on the membrane amounted to 94.3 ($\pm$ 11.6) percent of the total weight initially introduced on Side 1. The variance was too great to justify any attempt to calculate instantaneous rates of diffusion or true diffusion constants. Instead, it was chosen to define an arbitrary measure of diffusion tendency, called the <u>transfer factor</u>, as the average percent of initial charge on Side 1 transferred to Side 2 per day. This factor depends on the actual area of film used in the particular diffusion cell and upon the volume of liquid used as well as film thickness. Since the testing periods of all experiments were not all identical, this arbitrary transfer factor is only semi-quantitative and is intended to serve merely as a preliminary screening parameter.

<u>Typical Diffusion Curves; Effect of Polar Film Component</u>

The curves of Figure 2 serve to illustrate the change of Ag_2O concentrations in the half cells as a function of time. They also demonstrate the effect of a polar component upon the rapidity of silver diffusion. The C1, C3 and C5 films contain respectively 10, 30 and 50% by weight of the 1:1 copolymer of vinyl methyl ether and maleic anhydride, the remaining component being methyl cellulose. The arbitrary transfer factors, as defined in the preceding experimental section, are respectively 4.9, 8.3 and 14.9 for 30% KOH. The pickup of 30% KOH by these films after swelling is 40, 72 and 100% respectively and the corresponding electrolytic resistances are 73, 15 and 6.9 ohms-cm. respectively. Thus it is evident that increased concentration of the polar component decreases electrolytic resistance, increases swelling and also increases rate of silver ion diffusion. It will be shown below that treatments or compositions which increase electrolytic conductivity tend generally to increase the rate of silver diffusion.

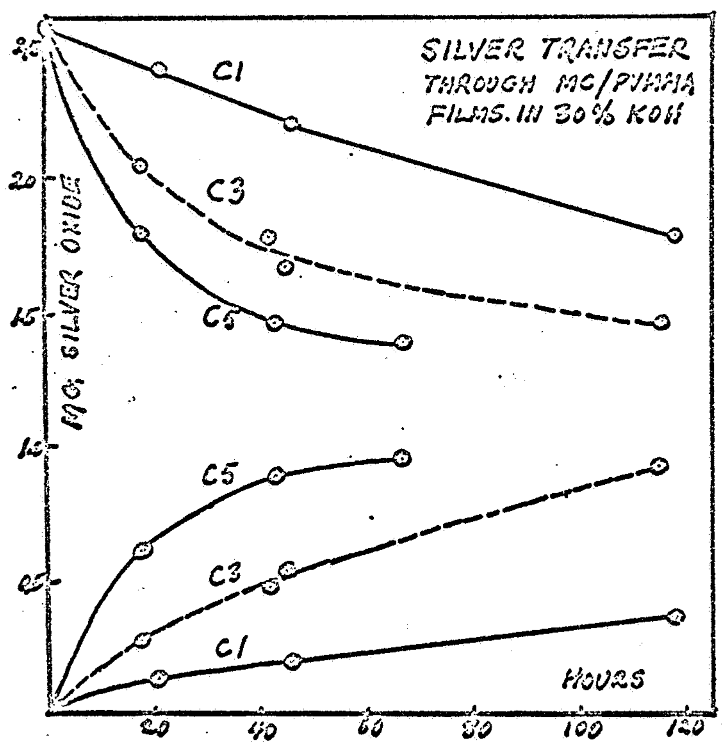

SILVER TRANSFER
THROUGH MC/PVMMA
FILMS. IN 30% KOH
C1
C3
C5
C5
C3
C1
MG. SILVER OXIDE
HOURS
20
40
60
80
100
120

Figure 2

Relationship Between Experiments Having Side 2 Starting Respectively With No Silver Ion and With Saturated Silver Oxide:

The numbers obtained for the distribution of radioactivity turn out to be essentially the same, within experimental error, regardless of whether Side 2 starts with a saturating concentration of non-labelled silver ion or with no silver ion at all. This can be better understood by consideration of the extreme cases (1) where the membrane completely stops silver by reacting with it and (2) where the membrane does not react at all but permits the silver ion to pass through at a measurable rate.

In the first case, the silver loss from Side 1, which is equal to the gain on the membrane from Side 1, is obviously the same regardless of the concentration of silver ion on Side 2. The partition of radioactivity will also be the same regardless of what is on Side 2. Of course, when Side 2 starts with the same concentration of silver ion as on Side 1, but unlabelled, then the amount of silver actually picked up by the membrane is twice the amount indicated by the radioactivity, since an equal amount of silver to that picked up from Side 1 is also picked up from Side 2.

Consider now the second extreme case, where the membrane has negligible reducing power. If the diffusion experiment is run with radioactively tagged silver ion on Side 1 and no silver ion on Side 2, the net transfer of silver ion will change at a rate which decreases asymptotically as the concentration gradient between Side 1 and Side 2 approaches zero. It is easy to see that at equilibrium both the total concentration of silver ion and the radioactivity will be equal to one half the original value on Side 1. What is not quite so obvious is that the rate with which the radioactivity equilibrium is attained also is essentially independent of the initial concentration of silver oxide on Side 2.

Let c_1 and c_2 be the concentrations of silver ion on Sides 1 and 2 respectively, s = the saturation concentration of silver ion, and c^* = the concentration of radioactive silver ion. Now if initially

$$c_1^* = c_o^*$$
$$c_1 = s$$

but

$$c_2^* = o$$
$$c_2 = o$$

that is, no silver ion of any kind on Side 2 to start.

$$\frac{c_o^*}{s} = f = \frac{c^*}{c} = \frac{c_1^*}{c_1} \quad \text{throughout the experiment}$$

$$\text{also} = \frac{c_2^*}{c_2} \quad \text{throughout the experiment}$$

Consider the point where

$$c_1^* = g\, c_o^* \tag{1}$$
$$c_2^* = (1-g)c_o^* \tag{2}$$
$$c_1 = \frac{gc_o^*}{f} \tag{3}$$
$$c_2 = (1-g)\,\frac{c^*}{f} \tag{4}$$

Now the rate r at which diffusion takes place from a particular side is proportional to the concentration on that side

$$r_1 = kc_1 \tag{5}$$
$$r_2 = kc_2 \tag{6}$$
$$r_1 - r_2 = k(c_1 - c_2) \tag{7}$$
$$r_1 - r_2 = k\,(2g-1)\frac{c_o^*}{f} \tag{8}$$

and the rate at which radioactivity is transferred from Side 1 to Side 2 is given by substituting $r_1 = r_1^*/f$. Therefore

$$r_1^* - r_2^* = k\,(2g-1)c_o^* \tag{9}$$

Compare now the case where Side 2 is initially also saturated with silver ion, but without radioactivity, i.e.

$$c_1^* = c_o^*$$
$$c_1 = s$$

and

$$c_2^* = o$$
$$c_2 = s$$

The overall diffusion process is constant at

$$r_1 - r_2 = k\,(s-s) = o$$
$$r_1 = r_2 = ks$$

But the ratio of radioactivity to total silver ion is no longer constantly equal to f. It now changes as Side 1 becomes depleted of radioactivity and Side 2 becomes enriched. Consider for this system the point where transfer has occurred to the conditions described by equation (1) and (2). Now

$$f_1 = \frac{gc_o^*}{s} \tag{10}$$

$$f_2 = \frac{(1-g)c_o^*}{s} \tag{11}$$

Since $r_1 = r_2 = ks$

$$r_1^* = f_1 r_1 = f_1 ks = kgc_o^* \tag{12}$$

$$r_2^* = f_2 r_2 = f_2 ks = k(1-g)c\ ^* \tag{13}$$

from which it follows that

$$r_1^* - r_2^* = k\ (2g-1)c_o^* \tag{14}$$

which is identical with equation (9). Thus it is evident that the rate of transfer has the same dependence on initial radioactivity on Side 1 regardless of whether Side 2 starts with zero concentration of silver oxide or saturation concentration. This relationship holds strictly only if no silver is reduced by the membrane since this would change the radioactivity available in solution in an unsymmetrical fashion. But if the amount of silver lost by reduction is relatively small, the curve of transfer with time soon assumes comparable slopes.

Experimental demonstration is given in Figure 15 (see page 32 in the Appendix) that with C3 film in 30% KOH, transfer of radioactivity follows the same time curve when Side 2 initially contains no silver ion as it does when Side 2 is initially saturated with untagged silver ion.

DATA & DISCUSSION

Silver Ion Diffusion and Related Properties of Oxidation-Resistant Types of Film

Data on films which are not readily oxidized by alkaline solutions of silver oxide are summarized in Tables I and II. The silver oxide lost per day to the exposed film during the diffusion experiment is in most cases well under one percent of the original silver oxide charged to the cell. Most of these films are modifications of methyl cellulose compositions. Also included are a polyvinyl pyridine-polyacrylic acid co-acervate, a methyl methacrylate-acrylate acid copolymer, a carboxy methyl methyl cellulose and an RAI treated polyethylene. The arbitrary transfer factors range from .24 to 15.8. Specific resistances and electrolyte pickup are also given.

In Figures 3 and 4, the logarithm of the measured electrolytic resistance has been plotted against the corresponding silver ion transfer factor. There is an obvious correlation between the tendency to conduct an electrolytic current and the permeability to silver ion.

TABLE 1. Silver Oxide Diffusion Through Membranes in 30% KOH Correlation with Electrolytic Resistance and With Electrolyte Pickup (Oxidation-resistant Types)

Composition (D)	Membrane #	Ag_2O Loss Per Day To Film % Orig. (A)	Diffusion Rate(C) Est. Side 1 Loss/ Day Ag_2O m	Side 2 Gain/ Day Ag_2O mg	Avg.1 + 2 Diffusion/day % of Orig. (A)	Resistance milli-ohms-in.^{2}	Specific Resistance ohms-cm swollen thickness	Electrolyte Pickup % Wt. Gain
Methyl Cellulose	0	.48	0	.012	.24	712	918.0	23.0
C1	1	1.87	.116	.134	4.86	72.8	88.1	40.0
C3	3	.29	.228	.196	8.3	15.2	15.2	70.0
C5	5	.80	.416	.335	14.9	6.9	5.85	100.0
MC 15% - 30%	12	.73	.216	.204	8.2	17.3	17.79	60.0
MC(-58°C.) - R.T.	18	.58	.127	.103	4.5	55.3	4.97	88.0
MC + 10% NaOH	7	.96	.198	.241	8.6	27.3	32.1	(32.)(B)
MC + 9% KOH	10	.57	.273	.144	8.2	41.6	55.0	(33.)
MC + 10% Me_4NOH	8	.35	.244	.308	10.7	21.8	31.3	(22.)
MC + 33% KOAc	15	.34	.117	.189	6.0	20.0	28.2	(20)
MC + 33% KOAc	15	.28	.167	.291	8.9	20.0	28.2	(20)
MC + 28% K Lactate	16	.19	.188	.241	8.4	18.8	17.96	(19)
C1 + 28% K Lactate	14	.42	.214	.166	7.4	18.8	20.84	(35)
C3A	6	.60	.337	.270	12.8	8.9	8.86	(70)
CMMC	11	.98	.186	.197	7.5	36.6	42.8	(45)
PVPyr-PAA	13	.14	.307	.370	13.2	10.1	9.4	82.0
MC + 32% K Succinate	9	.34	.314	.495	15.8	9.8	11.31	(38)
RAI 2.2 H	17	.95	.166	.081	4.8	24.5	47.8	-

Notes: (A) Ag_2O charged to cell, 2.56 mg. The number in this column is the arbitrary "transfer factor" defined on page 6.
(B) Values in parentheses are doubtful because of influence of extractable additives.
(C) For the total period of the tests. Average rate/day.
(D) For description of compositions see page 28, Table VII.

TABLE II. Silver Oxide Diffusion Through Membranes in 45% KOH
Correlation with Electrolytic Resistance (Oxidation-resistant Types)

Composition (D)	Membrane #	Ag_2O Loss Per Day To Film % Orig. (A)	Diffusion Rate(C) Est. Side 1 Loss/Day Ag_2O mg	Side 2 Gain/Day Ag_2O mg	Avg. 1 + 2 Diffusion/day % of Orig. (A)	Resistance milli-ohms-in.^{2}	Specific Resistance ohms-cm swollen thickness	Electrolyte Pickup-% Wt. Gain
C3 @ pH 2.8	3	.37	.107	.019	(1.91)	503	501.0	69
C3	3	.87	.655	.005	(1.05)(B)	503	501.0	69
C3 @ pH 6.2	19	.30	.128	.086	5.5	23.8	25.2	69
C3 @ pH 8.1	20	.29	.109	.098	5.4	18.8	21.1	51
C3A	6	.93	.134	.099	5.97	25.1	22.4	(68)(E)
MC + 9% KOH	10	.77	.095	.044	(3.54)	244.	333.0	(24)
MC + 10% Me_4NOH	8	.33	.121	.101	5.74	46.7	63.2	(34)
MC + 33% KOAc	15	.30	.127	.058	(4.8)	53.8	78.6	(22)
CI + 28% K Lactate	14	.31	.081	.042	(3.17)	68.6	74.4	(38)
PVPyr-PAA	13	.38	.066	.011	(2.0)	253.	310.0	38
Poly(MMA-AA)	21	.25	.138	.087	5.8	236.	26.1	-
MC + 32% K Succinate	9	.69	.174	.040	(5.53)	20.1	24.8	

Notes:
(A) Ag_2O charged to cell 1.935 mg. The number in this column is the arbitrary "transfer factor" defined on page 6.
(B) Values in parentheses indicate poor agreement of left cell loss with right cell gain.
(C) For the total period of the tests. Average rate/day.
(D) For full description of compositions see page 28, Table VII.
(E) Values in parentheses are doubtful because of influence of extractable additive.

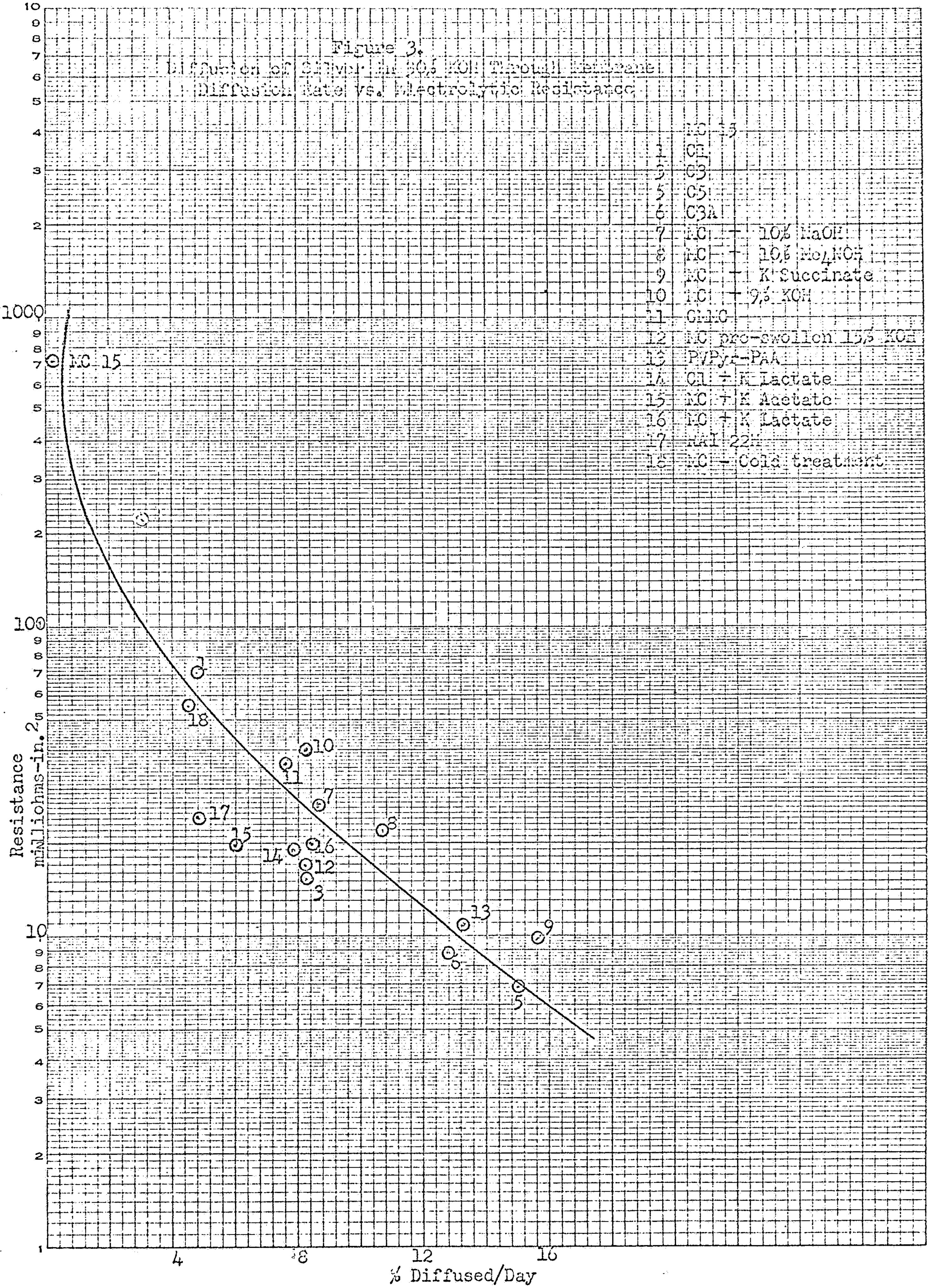


Figure 3.
Diffusion of Silver in 30% KOH Through Membrane
Diffusion Rate vs. Electrolytic Resistance
MC 15
1 C1
3 C3
5 C5
6 C3A
7 MC + 10% NaOH
8 MC + 10% Me4NOH
9 MC + K Succinate
10 MC + 9% KOH
11 CMC
12 MC pre-swollen 15% KOH
13 PVPy-PAA
14 C1 + K Lactate
15 MC + K Acetate
16 MC + K Lactate
17 RAI 22H
18 MC + Cold treatment
MC 15
Resistance milliohms-in.2
% Diffused/Day
1000
100
10
4
8
12
16

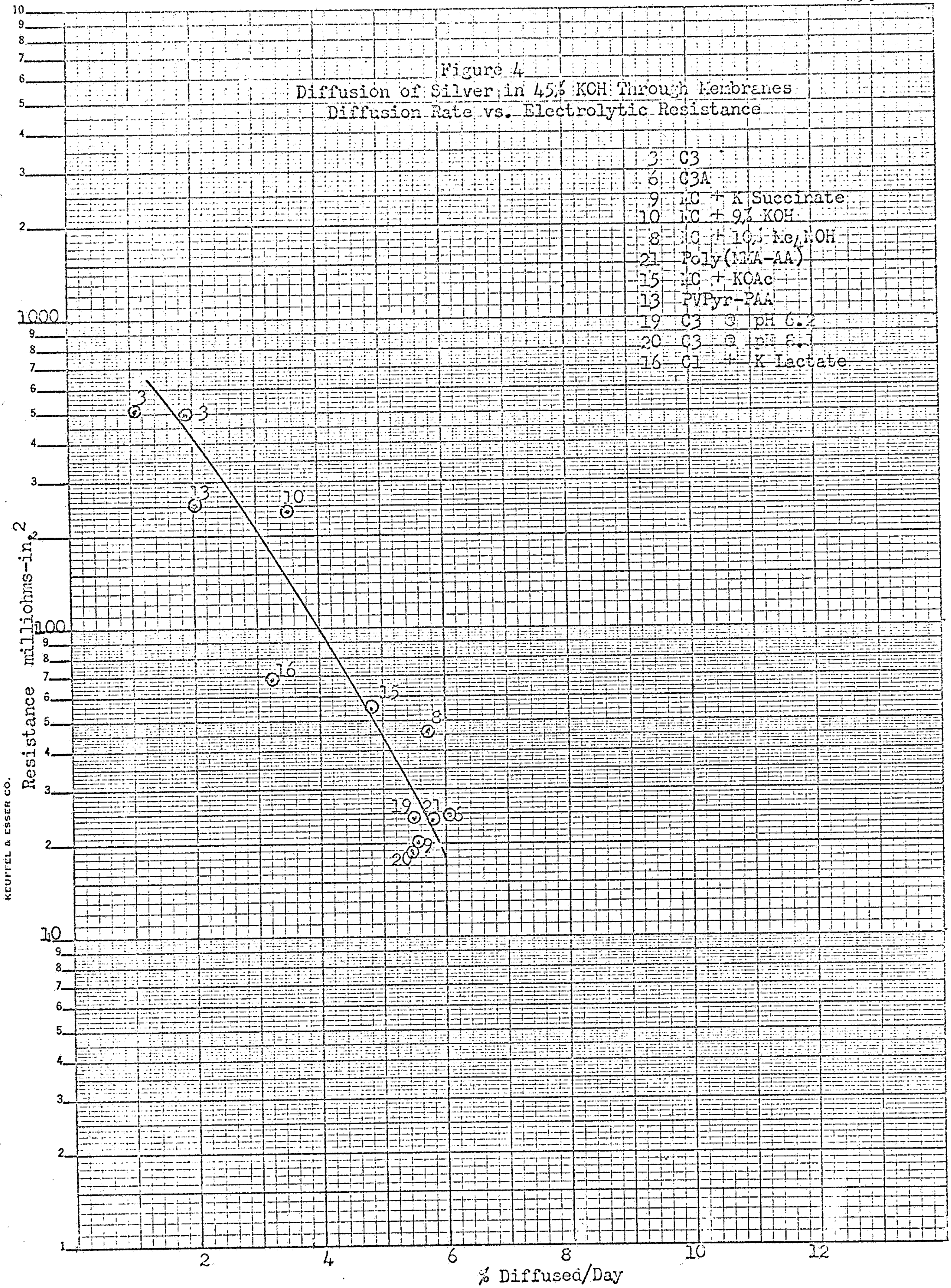


Figure 4
Diffusion of Silver in 45% KOH Through Membranes
Diffusion Rate vs. Electrolytic Resistance
3 C3
6 C3A
9 MC + K Succinate
10 MC + 9% KOH
8 MC + 10% Me_4NOH
21 Poly(MMA-AA)
15 MC + KOAc
13 PVPyr-PAA
19 C3 @ pH 6.2
20 C3 @ pH 8.1
16 C1 + K-Lactate
Resistance milliohms-in.^{2}
% Diffused/Day
1000
100
10
1
2
4
6
8
10
12
3
13
10
16
15
8
19
21
6
9
20
KEUFFEL & ESSER CO.

Diffusion of Ag_2O in 45% KOH Through Membranes of Oxidizable Types

Figure 5

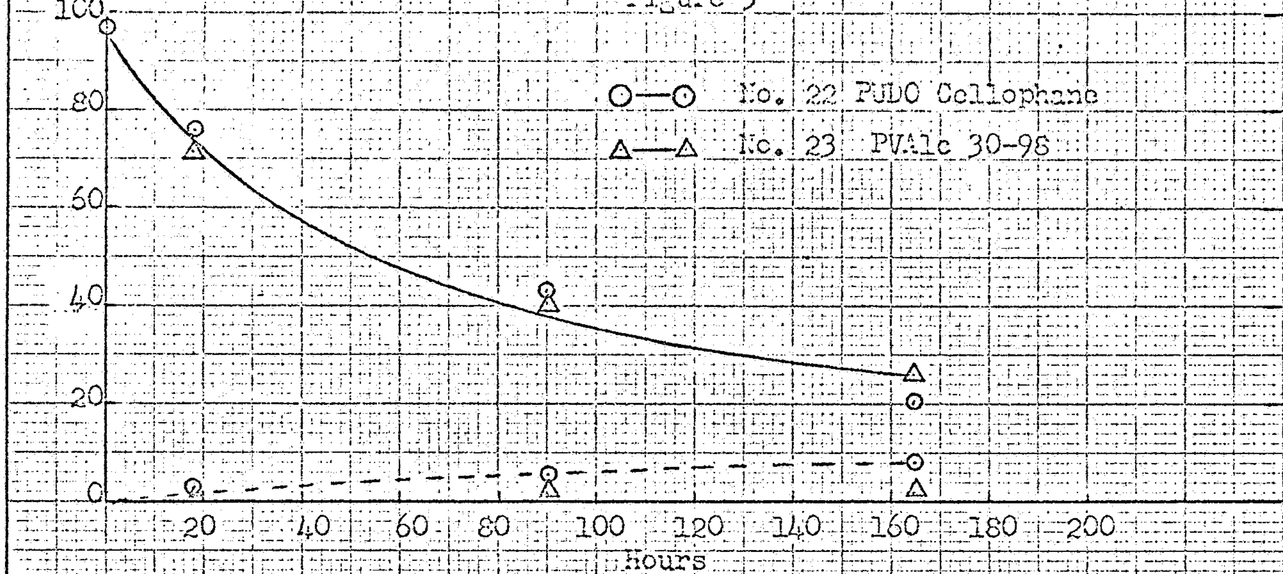
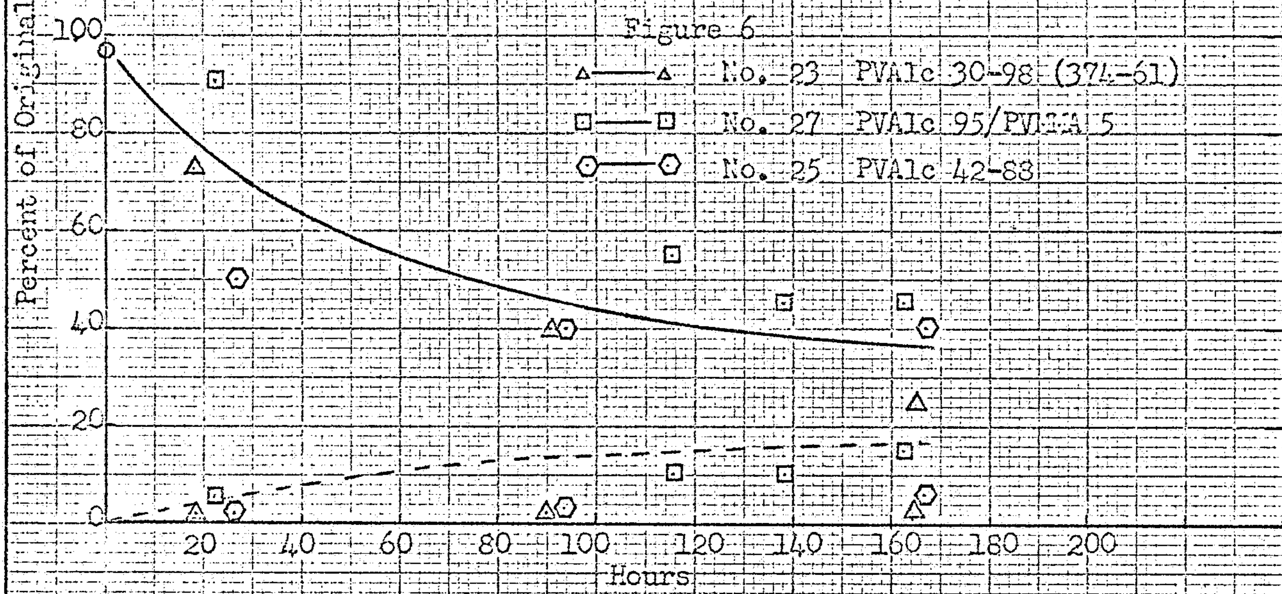


Figure 6



Readily Oxidizable Films

The membranes summarized in Table III comprise polymers which are readily oxidizable by alkaline silver oxide. They include cellophane, polyvinyl alcohol and hydroxyethyl cellulose, all of which have a high content of hydroxyl groups having the property of reducing agent. Films in which the oxidizable polymer predominates are very effective in stopping the passage of silver ion from Side 1 to Side 2 because the silver ion is reduced to metal and deposited as such on the membrane. When the content of oxidizable polymer is low, stoppage is lower, as in the case of "C5 + 20% PVAlc".

The laminate of PVAlc sandwiched between C3 layers holds back silver by the reducing action of the intermediate layer and the amount of silver eventually getting through to Side 2 is less than with C3 alone.

The lower pick-up of silver by the membranes in 45% KOH is related both to the lower concentration of silver ion in 45% KOH than in 30% KOH and to the lower swelling of the films with resultant lower accessibility of electrolyte liquid to the polymer substrate molecules.

Experimental diffusion data for various membranes of the oxidizable type are given in Figures 5 and 6. It is evident that silver ion appears in the solution of Side 2 more slowly than it disappears from Side 1, because a large portion of the silver ion reaching the membrane is reduced to metallic silver and is not available for further transfer.

TABLE III. Oxidation of Membranes During Diffusion Tests (Readily Oxidizable Types)

Composition	Membrane #	Duration of Test hours	Ag (A) on Film (B)			Ag_2O coming through (Side 2)			Resistance milli-ohms-in.
			Total mg	Per Day mg.	%/Day Orig. Ag_2O (C)	Total mg.	Per Day mg.	Per Day % Orig. Ag_2O (C)	
		In 30% KOH							
PUDO Cellophane		146	1.76	.288	11.3	.11	.018	0.7	7.6
PVAlc (30-98)	23	92	1.81	.472	17.5	.07	.018	0.7	24.7
PVAlc (30-98)	24	188	-	-	-	.60	.076	3.0	23.7
PVAlc (42-88)	25	188	-	-	-	.434	.055	2.1	25.6
PVAlc 98/PVMMA 2	26	91	1.73	.458	17.8	.057	.015	0.6	22.0
PVAlc 95/PVMMA 5	27	91	1.23	.325	12.7	.270	.071	2.7	16.5
PVAlc 80/PVMMA 20	28	-	-	-	-	-	-	-	5.5
E4*	29	66	1.76	.640	25.0	.08	.029	1.3	11.0
C5 + 20% PVAlc	30	41.5	.077	.0445	1.7	.68	.392	15.3	8.4
C3/PVAlc/C3**	31	66.0	.810	.294	11.5	.39	.142	5.5	13.5
		In 45% KOH							
PUDO Cellophane		164	.718	.105	5.4	.161	.0235	1.2	11.6
PVAlc (30-98)	23	164	.965	.141	7.3	.031	.0453	2.3	31.5
PVAlc (42-88)	25	166	.820	.118	6.1	.096	.014	0.7	
PVAlc 98/PVMMA 2	26	91.5	.486	.127	6.6	.264	.069	4.6	28.1
PVAlc 95/PVMMA 5	27	162	.219	.032	1.7	.331	.049	2.5	18.2
PVAlc 80/PVMMA 20	28	115	.200	.042	2.15	.487	.115	5.9	8.2
C5 + PVAlc	30	89.5	.143	.038	2.0	.109	.029	1.5	77.9
C3/PVAlc/C3**	31	89.5	.437	.117	6.0	.032	.009	0.5	253.

Notes:
(A) Calcd. as Ag_2O.
(B) Orig. Ag_2O charged to Cell (in 30% KOH 2.56 mg;)in 45% KOH 1.935 mg
(C) The number in this column is the arbitrary "transfer factor" defined on page 6.

* E4 is 40 parts by weight Hydroxyethyl Cellulose (Union Carbide QP09) and 60 parts Methyl Cellulose (Methocel 15).

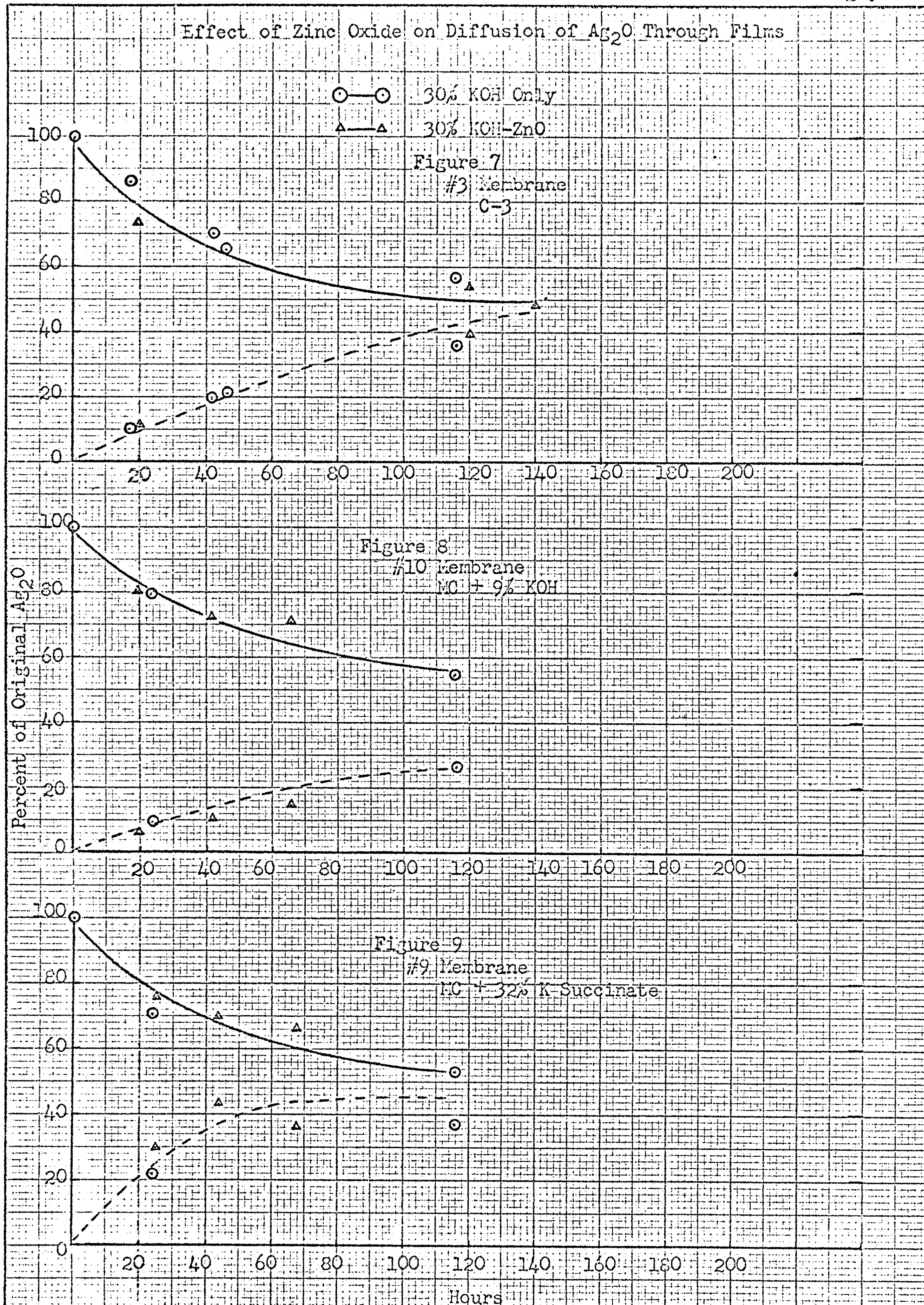
** This is a triple laminate film.

Silver Diffusion in 30% KOH Saturated with Zinc Oxide

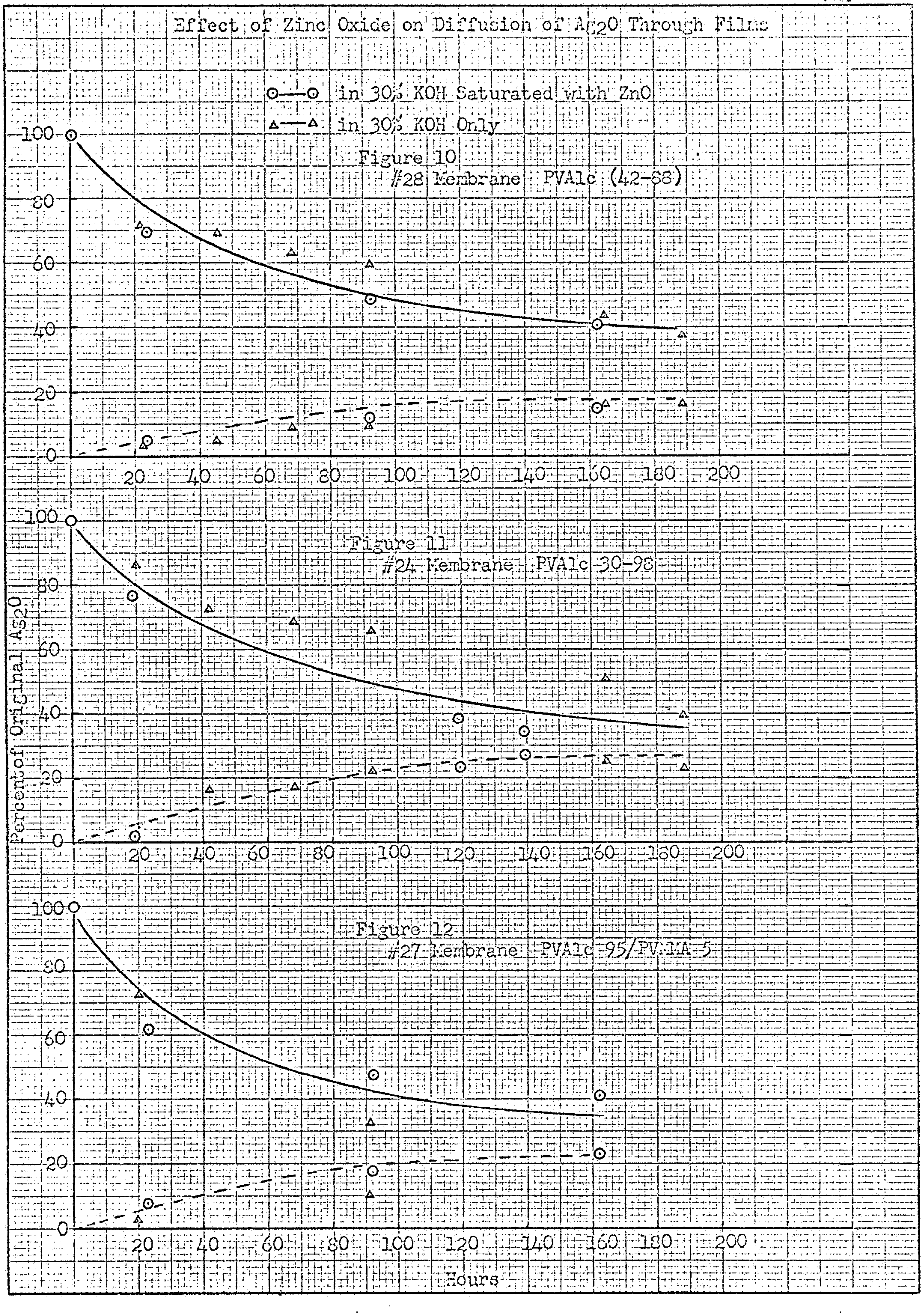
Since the electrolyte of commercial silver-zinc cells is usually saturated with zinc oxide, forming a zincate solution, it is of interest to know how silver ion diffusion may be affected by the presence of zincate. The diffusion of silver ion through eight representative films was studied using 30% potassium hydroxide saturated with zinc oxide as the electrolyte.

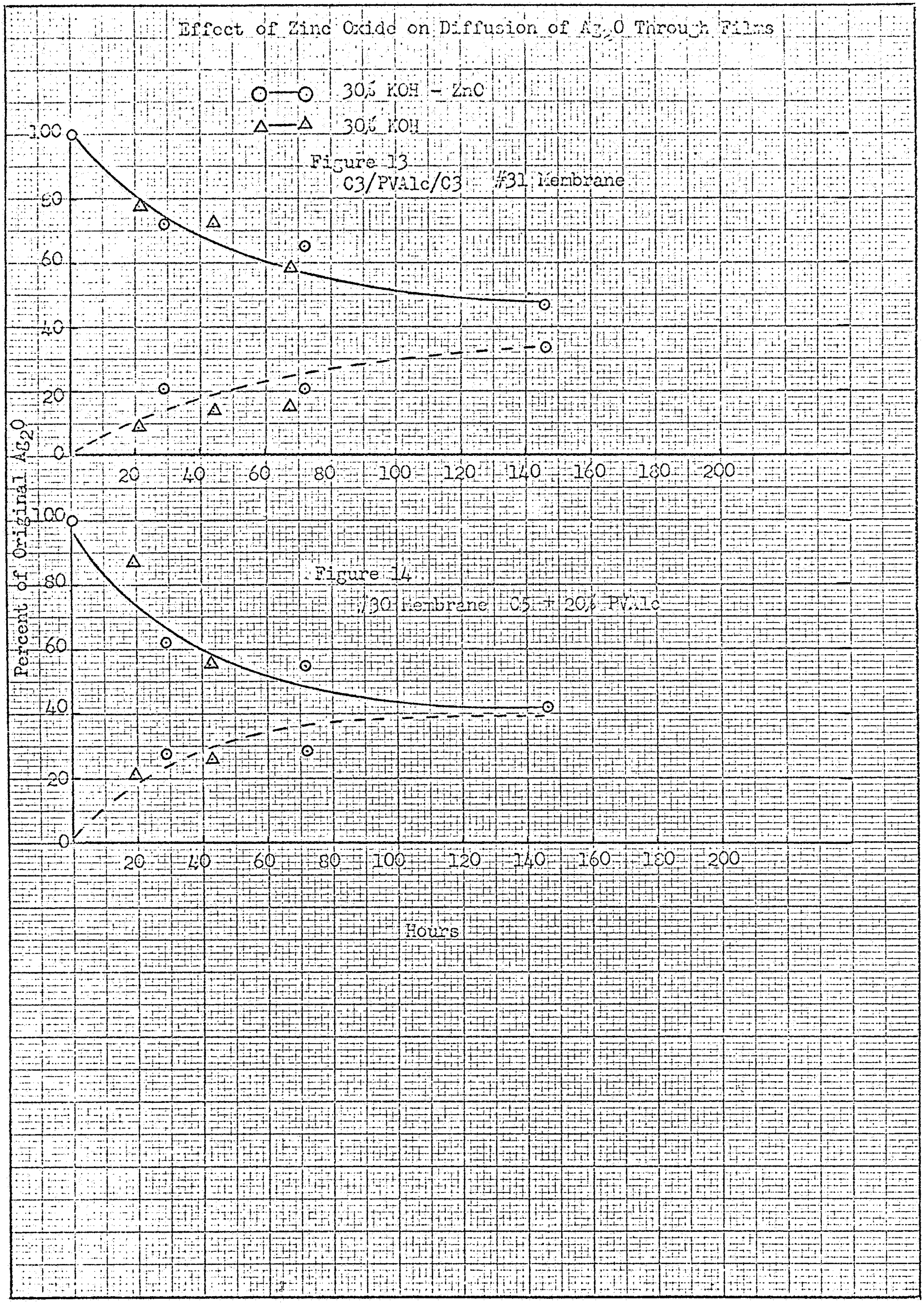
A solution of 30% KOH saturated with radioactively tagged silver oxide was prepared as described above under "Experimental Procedure". Both this solution and a plain 30% KOH solution were respectively saturated with zinc oxide by stirring with excess zinc oxide and filtering.

Experimental data on the selected films in ZnO-saturated KOH are plotted in Figures 7 through 14 along with corresponding data on the same films in 30% KOH without ZnO. It is obvious from these that, within experimental error, the presence of zincate has no significant effect on the silver diffusion. It may therefore be assumed that all the data on silver diffusion in 30% KOH would apply also to the corresponding electrolyte solutions saturated with zinc oxide.



Effect of Zinc Oxide on Diffusion of Ag_2O Through Films
30% KOH Only
30% KOH-ZnO
Figure 7
#3 Membrane
C-3
Figure 8
#10 Membrane
MC + 9% KOH
Figure 9
#9 Membrane
MC + 32% K-Succinate
Percent of Original Ag_2O
0
20
40
60
80
100
120
140
160
180
200
Hours


Effect of Zinc Oxide on Diffusion of Ag2O Through Films
in 30% KOH Saturated with ZnO
in 30% KOH Only
Figure 10
#28 Membrane PVAlc (42-88)
Figure 11
#24 Membrane PVAlc 30-98
Figure 12
#27 Membrane PVAlc 95/PVMA 5
Percent of Original Ag2O
Hours
0 20 40 60 80 100
20 40 60 80 100 120 140 160 180 200


Effect of Zinc Oxide on Diffusion of Ag_2O Through Films
30% KOH - ZnO
30% KOH
Figure 13
C3/PVAlc/C3 #31 Membrane
Figure 14
#30 Membrane C5 + 20% PVAlc
Percent of Original Ag_2O
Hours
0
20
40
60
80
100
120
140
160
180
200

The effect of saturation with zinc oxide on electrolytic resistance is shown in Tables IV, V and VI. Resistance in 30% KOH is moderately increased by the presence of zincate. In 45% KOH, however, resistances are increased several-fold by the presence of zincate, the factor varying from 1.4 to 4.5. It is therefore possible that in 45% KOH the presence of zincate may also have an appreciable effect on the rate of silver diffusion. Time was not available for silver diffusion experiments in 45% KOH with zincate.

Information is given in Table V on the weight increase of some of the films after exposure to 30% KOH respectively without and with zincate. There is no significant difference.

TABLE IV. - Effect on Resistance of Saturating 30% KOH with ZnO

Membrane No.	Composition	Dry Thickness mils	Resistance milliohms-in.^{2} 30% KOH-ZnO	30% KOH	Specific Resistance ohms/swollen thickness 30% KOH-ZnO mils*	ohms-cm	30% KOH mils*	ohms-cm
3	C3	1.5	18.05	16.1	2.55	18.0	2.55	16.0
24	PVAlc (30-98)	1.6	34.0	22.6	3.05	28.3	3.05	18.8
25	PVAlc (42-88)	1.5	36.1	25.6	2.60	35.2	2.60	25.0
27	PVAlc (42-88)95/ PVMMA 5	1.5	25.8	16.5	2.97	22.0	2.91	14.4
10	MC + 9% KOH	1.5	62.9	41.6	2.00	78.5	1.77	59.6
9	MC + 32% K Succinate	1.6	12.0	10.4	2.20	13.8	2.20	12.0
30	C5 + 20% PVAlc (42-88)	1.4	8.4	8.4	3.86	5.5	4.00	5.3
31	C3/PVAlc/C3	1.5 (?)	16.9	13.5	2.50	17.2	2.50	13.7
23	PUDO Cellophane	1.0	11.2	7.6	3.42	8.3	3.30	5.9
1	C1	1.5	97.4	71.3	2.19	118.	2.10	86.
15	MC + K Acetate	1.5	29.6	20.0	1.95	38.5	1.80	27.3
8	MC + 10% Me KOH	1.4	22.0	21.8	1.78	31.4	1.80	36.7
14	C1 + 28% K Lactate	1.7	35.3	18.8	2.30	39.0	2.30	20.7

Note:

* Swollen thickness calculated from weight electrolyte absorbed.

TABLE V. Effect of ZnO on Resistance and Swelling of Films - 30% KOH

Membrane No.	Composition	30% KOH (A) Resistance milliohms-in.^{2}	Wt. Increase %	30% KOH, Sat'd. with ZnO (B) Resistance milliohms-in.^{2}	Wt. Increase %
1	C1	71.3	40.	97.9	46
3	C3	16.1	72	18.	71.
10	MC + 90% KOH	41.6	28	62.9	34
15	MC + 33% K Acetate	20	(20)	29.6	(30)
9	MC + 32% K Succinate	10.4	(38)	12.0	(38)
24	PVAlc 30-98	22.6	92	34.0	91
25	PVAlc 42-88	256.	74	32.7	73
27	PVAlc (42-88) 95/ PVMMA 5	16.5	94	25.8	98
28	PVAlc (42-88) 80/ PVMMA 20	8.4	87	8.4	76
22	PUDO Cellophane	7.6	230.	11.2	242.

Notes: (A) Sp. g. 1.29

(B) Sp. g. 1.32

TABLE VI. - Effect on Resistance of Saturating 45% KOH with ZnO

Membrane No.	Composition	Dry Thickness mils	Resistance milliohms-in.^{2} 45% KOH-ZnO	45% KOH	Specific Resistance ohms/swollen thickness 45% KOH-ZnO mils*	ohms-cm	45% KOH mils*	ohms-cm
22	PUDO Cellophane	1.0	19.6	11.6	3.1	16.1	3.0	9.8
14	C1 + 28% K Lactate	1.7	225.	68.6	2.6	220.	2.6	66.9
10	MC + 9% KOH	1.5	340.	244.	2.2	393.	2.2	282.
25	PVAlc 42-88	1.6	46.7	29.0	3.2	37.1	3.2	11.6
23	PVAlc 30-98	1.7	43.9	31.5	2.4	46.5	3.4	23.1
27	PVAlc (42-88) 95/ PVMMA 5	1.6	38.9	18.2	3.0	33.8	3.7	12.5
15	MC + 33% K Acetate	1.4	249.	53.8	1.8	351.	1.7	76.
8	MC + 10% Me_4NOH	1.3	92.5	61.7	1.6	147.	1.6	98.
3	C3	1.6	485.	503.	2.3	536.	2.3	555.

APPENDIX

The composition of the membranes whose silver barrier properties are the subject of this report are summarized in Table VII. The accounting of radioactively tagged silver is summarized in Tables VIII, IX and X.

Figures 15 through 23 present diffusion curves for representative films.

In Figure 15 it is shown that transfer of radioactivity through C3 films follows the same curve regardless of whether the opposite side initially contains no silver ion or is initially saturated with untagged silver ion. This is an experimental illustration of the principle derived on pages 8 to 10 of this report.

In Figure 16 it is shown that the two kinds of swelling treatments which successfully increase the conductivity of unmodified methyl cellulose also increase the rate at which silver ion diffuses through the film. The films of this figure are respectively #0, straight methyl cellulose; #12 which was equilibrated first in 15% KOH, then in 30% KOH; and #18 which was pre-swollen by cooling in 30% KOH at -58° C, then returned to room temperature. Data on electrolytic resistance and electrolyte absorption of these films are included in Table I.

In Figure 17, a comparison is made of silver ion diffusion curves for the same film in different concentrations of potassium hydroxide. The particular film compared is No. 13, a co-acervate of polyvinyl pyridine and polyacrylic acid. Similar sensitivity to concentration was likewise exhibited by all membranes in the C-series including No. 3 and No. 5, also by No. 10 film which is methyl cellulose 100 parts, potassium hydroxide 9 parts. The curves show that a higher percentage of the available silver oxide diffuses in a 30% KOH system than in a 45% KOH system. However, inasmuch as the saturation concentrations for silver oxide in 30% vs. 40% KOH are in the ratio 2.56 to 1.94, the actual diffusion in weight of silver oxide per unit time is not quite so great. For example, when 20% of the silver oxide in 30% KOH diffuses in the same time as 10% of the silver oxide in 45% KOH, the total amount of diffused silver oxide is 13 to 1.

The increased silver ion permeability in the more dilute potassium hydroxide is in agreement with the increased swelling and conductivity. As the data in Tables I and II show, on changing from 45% to 30% KOH, the specific resistance of No. 13 film changes from 310 to 9.4 ohms-cms. and the electrolyte pickup changes from 38 to 82%.

Figure 18 shows the effect on silver ion diffusion brought about by incorporating potassium hydroxide in the casting solution of C3 membranes. The diffusion tests were run in 45% KOH solution. It is evident that the increase in pH of casting solution from 2.8 to 6.2 results in a significant increase in permeability to silver ion. This corresponds to a decrease in electrolytic resistance from 501 to 25 ohm-cms, as the data in Tables II and IX show. Diffusion data are not sufficiently precise to detect further increase in permeability by additional increases of casting solution pH to 8.1. However the aforementioned tables show that electrolytic resistance was further reduced to 21 ohms-cms.

TABLE VII. - Composition of Membranes Used in Diffusion Tests

No.	Description	Lot No.	Dry Thickness mils
0	MC15 Methyl cellulose 15 cps (Dow)	485-118	1.6
1	C1 10% PVMMA (polyvinyl methyl ether-maleic anhydride), 90% MC15	421-116	1.5
3	C3 30% PVMMA, 70% MC 15	499-15	1.5
5	C5 50% PVMMA, 50% MC 15	445-140	1.5
6	C3A C3 + 10% 3-hydroxypropylamine	499-30	1.5
7	MC15 + 10% NaOH	504-134	1.5
8	MC15 + 10% Me_4NOH (tetramethyl ammonium hydroxide)	545-64	1.4
9	MC15 + 32% potassium succinate	534-127	1.6
10	MC15 + 9% KOH	522-62	1.5
11	CMMC Carboxymethyl methyl cellulose (Borden prep.)	483-5	1.5
12	MC15 membrane pre-swollen in 15% KOH, then equilibrated in 30% KOH	534-30	1.5
13	PVPyr-PAA Coacervate membrane of polyvinyl pyridine and polyacrylic acid	482-127	1.5
14	C1 + 28% Potassium lactate	522-119	1.7
15	MC15 + 33% Potassium acetate	534-63	1.5
16	MC15 + 28% Potassium lactate	534-67	1.4
17	RAI 2.2H Graft polymer poly(ethylene-acrylic acid) (Radiation Appl. Lab)		1.5(?)
18	MC15 membrane precooled in 30% KOH at -58° C.	562-11	1.5
19	C3 + KOH to pH 6	563-23	1.5
20	C3 + KOH to pH 8	563-24	1.5
21	Poly(methyl methacrylate-acrylic acid) (Borden prep.)	563-59	1.5
22	Cellophane PUDO	-	1.0
23	PVAlc (polyvinyl alcohol, 30 viscosity, 98% hydrolyzed)	374-61	1.5
24	PVAlc (" " " " " "	495-65	1.6
25	PVAlc (polyvinyl alcohol, 42 viscosity, 88% hydrolyzed)	534-105	1.5
26	PVAlc (42-88) 98%, PVMMA 2%	534-63	1.5
27	PVAlc (42-88) 95%, PVMMA 5%	545-62	1.5
28	PVAlc (42-88) 80%, PVMMA 20%	545-43	1.5
29	E4 (hydroxyethyl cellulose 35%, MC15 65%)	421-109	1.6
30	C5 + 20% PVAlc (42-88)	534-24	1.4
31	Triple laminate membrane C3/PVAlc (30-98)/C3	445-105	1.5(?)

Note:
(?) denotes irregular surface. Exact thickness not known.

TABLE VIII. Diffusion Through Membranes of Ag_2O in 30% KOH
Distribution of Silver

Membrane #	Composition	Period of Test hrs	Disposition of Silver (Ag_2O) at End of Expt. (init. 2.57 mg) Side 1 mg	Side 2 mg	On membrane mg	Total mg.	Acc'd. for % of Orig.	Resistance milliohms-in.^{2}	Specific Resistance ohms-cm. swollen thickness
0	MC 15	89.5	2.770	.047	.046	2.863	111.5	712.	918.0
1	C1	116	2.160	.370	(.230)	2.76	107.7	72.8	88.1
3	C3	115	1.468	.938	.036	2.44	95.7	15.2	15.2
5	C5	67	1.400	.962	.058	2.42	94.5	6.9	5.85
6	C3A	90	1.295	1.010	.058	2.363	92.3	8.9	8.86
7	MC15 + 10% NaOH	116	1.608	1.161	.116	2.88	112.8	27.3	32.1
8	MC15 + 10% Me_4NOH	116	1.637	1.160	.034	2.83	110.5	21.8	31.3
9	MC15 + K Succinate	67.5	1.685	.930	.025	2.64	103.0	9.8	11.31
10	MC15 + 9% KOH	65	1.820	.390	.040	2.25	87.8	41.6	55.0
11	CMMC	67.5	2.040	.551	.070	2.667	104.0	36.6	42.8
12	MC15 15% 30%	89.5	1.755	.762	.070	2.587	101.0	17.3	17.79
13	PVPyr-PAA	67.5	1.705	1.028	.010	2.743	107.0	10.1	9.4
14	C1 + K Lactate	65	1.98	.450	.03	2.46	96.2	18.8	20.89
15	MC15 + K Acetate	162	1.77	1.28	.058	3.108	121.3	20.0	28.2
16	MC15 + K Lactate	90.5	1.847	.936	.019	2.802	109.4	18.8	17.96
17	RAI 2.2 H	162	1.442	.544	.168	2.154	84.2	24.5	47.8
18	MC15 -58°C; +25°C	162	1.698	.678	.100	2.476	96.8	55.3	4.97
22	PUDO Cellophane	146	.543	.11	1.76	2.413	94.3	7.6	6.6
23	PVAlc 30-98	92	1.080	.07	1.81	2.96	115.3	24.7	22.0
24	PVAlc 30-98	188	1.037	.60	-	-	-	23.7	19.6
25	PVAlc 42-88	188	.975	.43	-	-	-	25.6	26.6
26	PVAlc 98/PVMMA 2	91	.708	.057	1.73	1.495	97.2	22.6	20.7
27	PVAlc 95/PVMMA 5	91	.840	.270	1.23	2.349	92.0	16.5	14.1
29	E4	66	.720	.08	1.76	2.56	100.0		9.1
30	C5 + 20% PVAlc	41.5	1.435	.68	.077	2.192	85.5	8.4	7.6
31	C3/PVAlc/C3	66	1.530	.39	.810	2.73	106.7	13.5	13.19

TABLE IX. Diffusion Through Membranes of Ag_2O in 45% KOH
Distribution of Silver

Membrane #	Composition	Period of Test hrs	Disposition of Silver (Ag_2O) at End of Expt. (A) Side 1 mg	Side 2 mg	On membrane mg	Total mg.	Acc'd. for % of Orig.	Resistance milli-ohms-in.^{2}	Specific Resistance ohms-cm swollen thickness
3	C3	68	1.632	.053	.106	1.691	87.6	503	501
3	C3	192	1.495	.040	.134	1.669	86.3	503	501
19	C3 @ pH 6.2	163	1.067	.584	.039	1.690	87.3	23.6	25.2
20	C3 @ pH 8.1	163	1.195	.668	.038	1.901	98.1	19.0	21.1
6	C3A	115	1.293	.473	.086	1.852	95.6	28.1	22.4
10	MC + 9% KOH	162	1.295	.275	.100	1.670	86.4	244	333.0
8	MC + Me_4NOH	91.5	1.402	.387	.024	1.803	93.3	46.7	63.2
15	MC + 33% KOAc	162	1.075	.393	.039	1.507	77.8	53.8	78.6
9	MC + 32% K Succinate	68	1.443	.113	.038	1.594	82.5	20.1	24.8
14	C1 + 28% K Lactate	192	1.288	.336	.047	1.671	86.5	68.6	74.4
21	Poly(MMA-AA)	166	.977	.603	.035	1.616	83.5	23.6	26.1
13	PVPyr-AA	162	1.490	.074	.050	1.614	83.3	253.	310.0
22	PUDO Cellophane	164	.427	.152	.683	1.262	65.3	11.6	8.74
23	PVAlc (30-98)	164	.512	.029	.915	1.456	75.3	31.5	21.6
25	PVAlc (42-88)	166	.810	.096	.820	1.726	89.0	29.0	22.3
26	PVAlc 98/PAA 2	91.5	1.150	.264	.486	1.910	98.8	28.1	20.5
27	PVAlc 95/PAA 5	162	.936	.331	.219	1.486	76.8	18.2	12.5
28	PVAlc 80/PAA 20	115	1.350	.487	.200	2.037	104.0	8.2	4.04
30	C5 + 20% PVAlc	89.5	1.140	.109	.143	1.392	72.0	77.9	66.3
31	C3/PVAlc/C3	89.5	1.226	.032	.437	1.695	87.6	253.	306.0

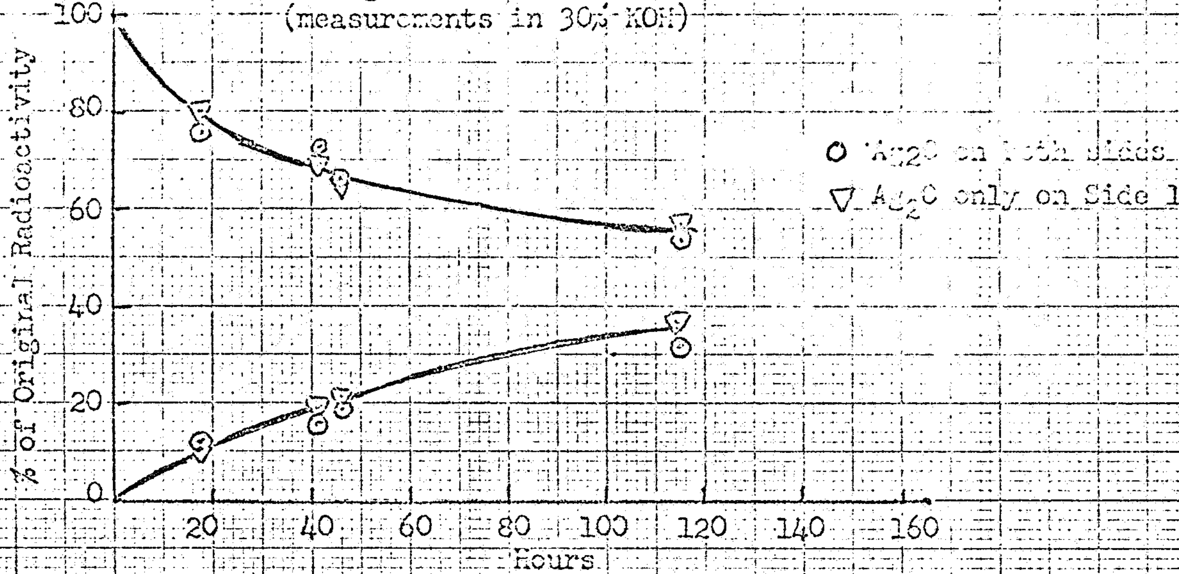
(A) Initial charge to Side 1 was 1.935 mg.

TABLE X. Distribution of Silver (A) at Termination of Diffusion Tests (30% KOH, Saturated with Ag_2O, then Zinc Oxide)

Reference 549-	Composition	Hours	Calcd. mg. Ag_2O Side 1	Side 2	On Film	Total	Accounted for %	Elec. Resistance in this medium milli-ohms-in^2	Specific Resistance ohms-cm Swollen thickness
64	C3	139	.721	.707	.006	1.431	97.1	18.0	24.12
68	MC + 9% KOH	115	.818	.386	.013	1.217	82.2	62.9	83.0
69	MC + K Succinate	115	.784	.558	.005	1.352		12.0	13.22
77	PVAlc (42-88)	162	.617	.222	.267	1.106	75.1	36.1	32.74
68	PVAlc (30-98)	139	.513	.400	.430	1.343	88.7	34.0	27.86
76	PVAlc (42-88) 95/PVMMA 5	162	.616	.351	.134	1.101	74.6	25.8	22.4
72	C5 + 20% PVAlc	145	.640	.621	.008	1.269	86.2	8.4	8.84
73	C3/PVAlc/C3	145	.710	.514	.022	1.246	84.5	16.9	20.45

(A) 30% KOH was saturated with Ag_2O at 57 mg/liter of solution. To the filtered solution .005 ml radioactive $AgNO_3$ in 2 ml. 30% KOH was added. The mixed solution was filtered and radioactive count taken as the measurement of silver oxide present based on assumption of total saturation. Aliquots of this were saturated with zinc oxide to make up the stock used in these experiments. Solubility of zinc oxide was found to be 57 grams/liter. Silver oxide by radioactive count was 32.8 milligrams/liter. The amount of Ag_2O charged to cells (45 ml volume) was therefore 1.473 mg.

Figure 15 - Transfer of Radioactivity on Ag_2O Diffusion Through C3 Film (measurements in 30% KOH)



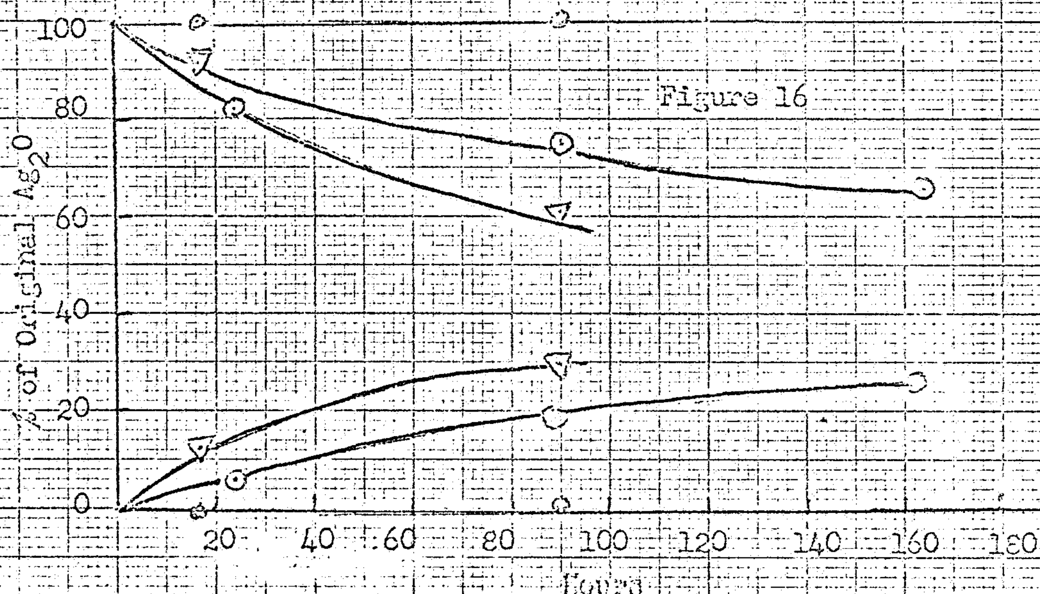


Figure 16 - Effect of Pre-swelling Treatments on Ag_2O Diffusion Through Straight Methyl Cellulose (measurements in 30% KOH)

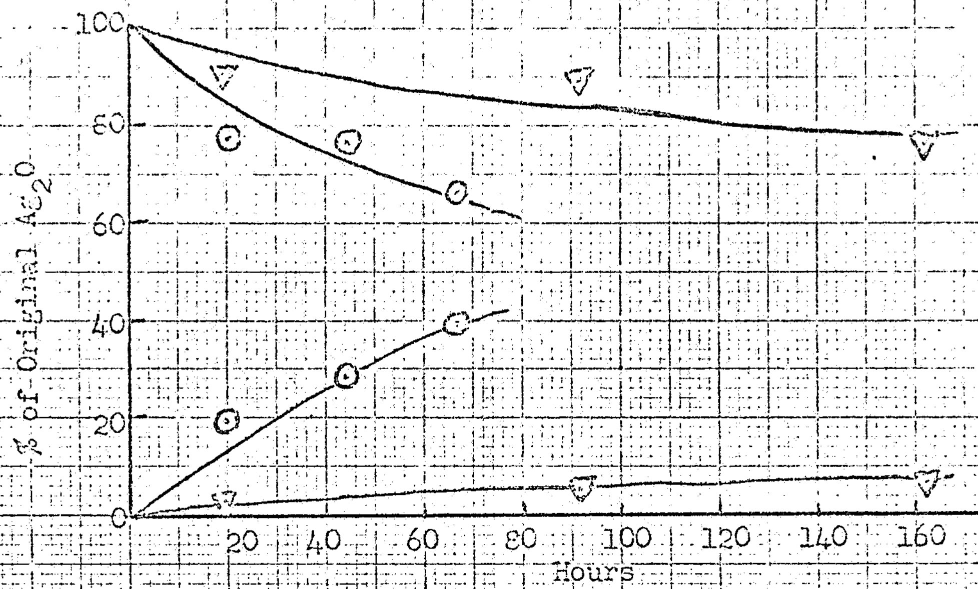


Figure 17 - Comparison of Silver Ion Diffusion Through PVPy-PAA Co-acervate Film No. 13 in 30% KOH vs. 45% KOH

⊙ 30% KOH

▽ 45% KOH

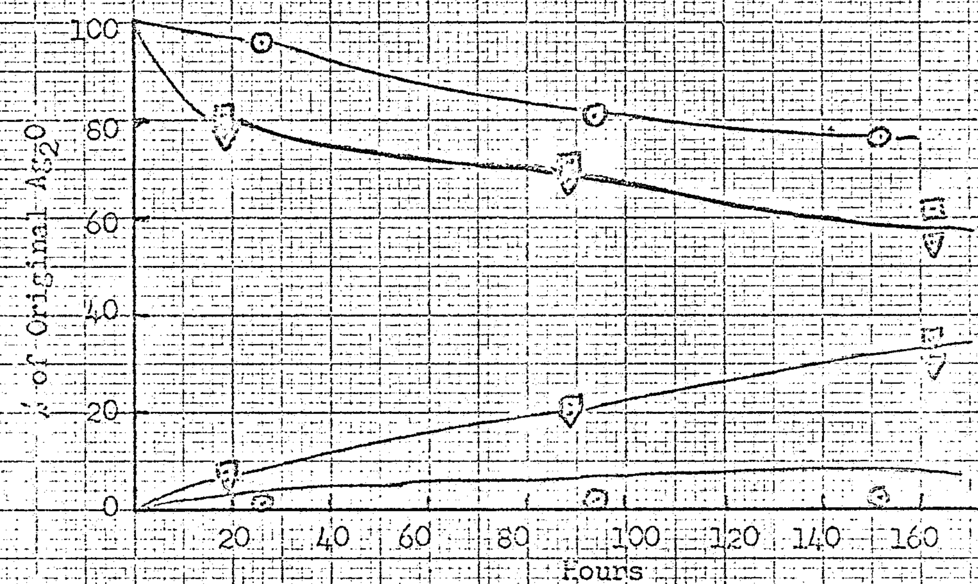


Figure 18 - Effect of Potassium Hydroxide Incorporation in Casting Solutions of C3 Membrane on Silver Ion Diffusion in 45% KOH

⊙ Film No. 3 Cast at pH 2.8

▽ Film No. 19 Cast at pH 6.2

⊡ Film No. 20 Cast at pH 8.1

Figure 19 shows the silver ion diffusion curves obtained for No. 21 acrylate membrane in 45% KOH. The relatively slow appearance of silver ion on Side 2 compared with the rate of loss on Side 1 is inconsistent with the finding recorded in Table IX that this membrane does not pick up silver by oxidation. This is probably due to experimental error and further interpretation should be withheld pending repeat experiments.

Figure 20 shows the silver ion diffusion curves for No. 25 polyvinyl alcohol 42-88 in 45% KOH. Here the extremely slow appearance of silver on Side 2 compared to the rate of loss from Side 1 is consistent with the observation that considerable silver is deposited on the membrane by oxidation.

Figures 21, 22 and 23 respectively present silver diffusion data obtained respectively on No. 17 RAI film, No. 8 film made from methyl cellulose modified with tetramethyl ammonium hydroxide, and No. 11 film made from Borden experimental carboxy methyl methyl cellulose.

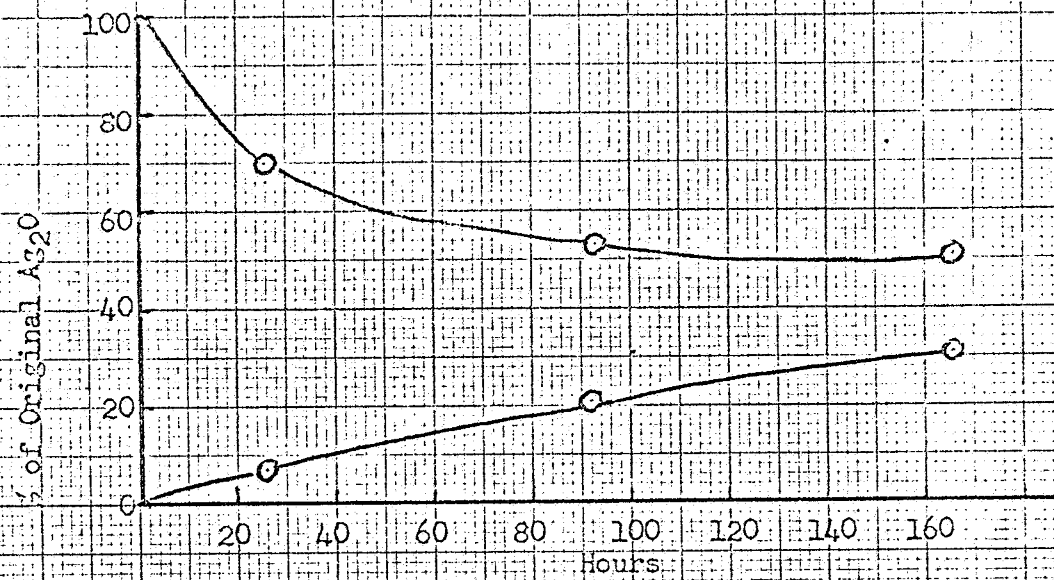


Figure 19 - Silver Diffusion Curves in 45% KOH
for Polyacrylate Film No. 21

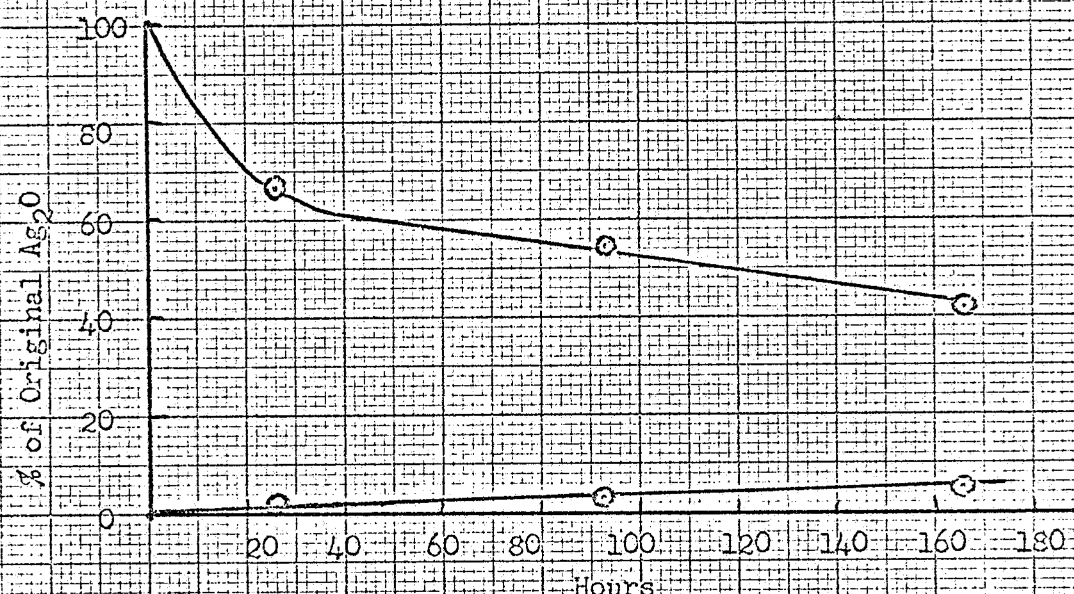
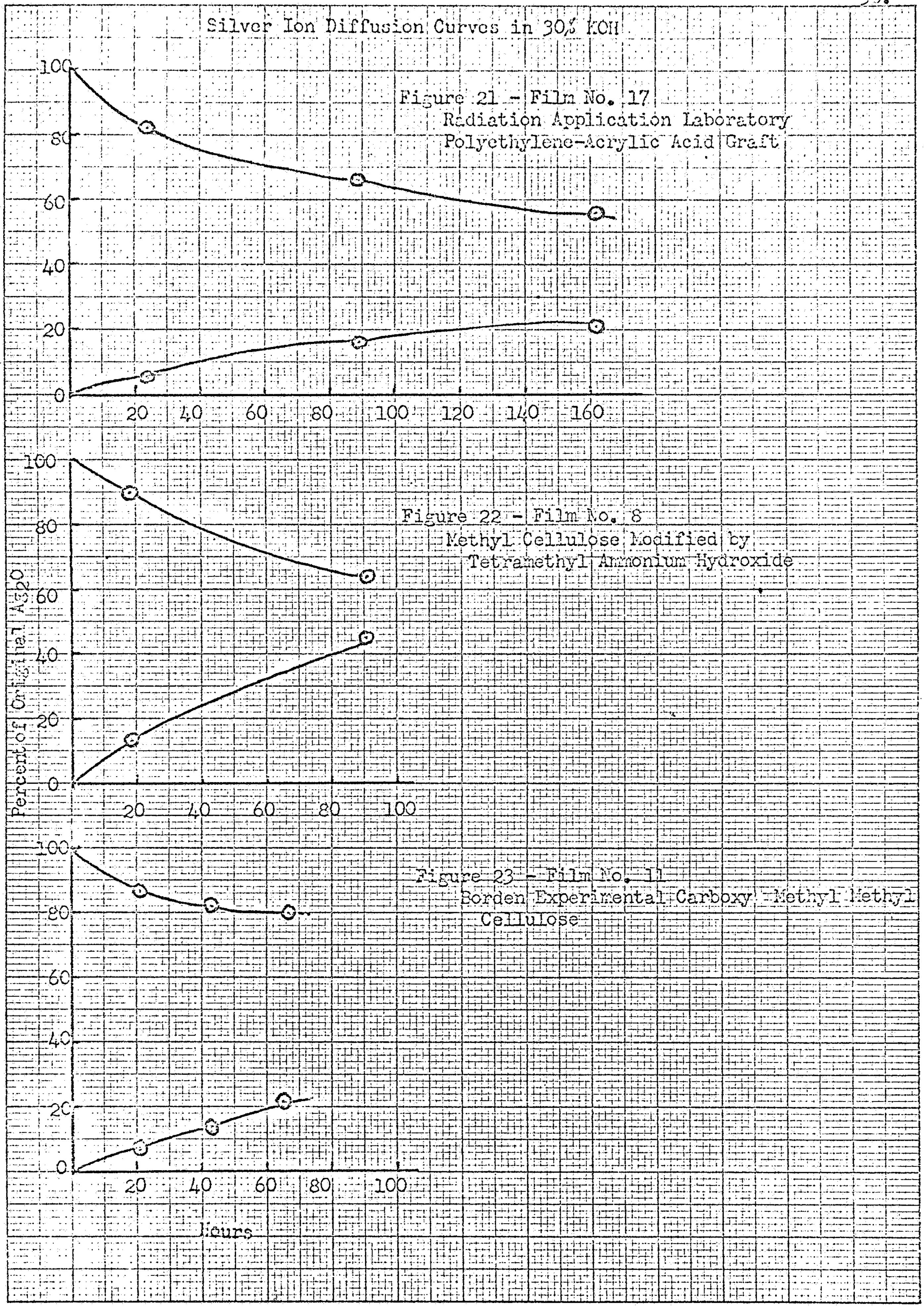


Figure 20 - Silver Diffusion Curves in 45% KOH
for Polyvinyl Alcohol Film No. 25


Silver Ion Diffusion Curves in 30% KOH
Figure 21 - Film No. 17
Radiation Application Laboratory
Polyethylene-Acrylic Acid Graft
Figure 22 - Film No. 8
Methyl Cellulose Modified by
Tetramethyl Ammonium Hydroxide
Figure 23 - Film No. 11
Borden Experimental Carboxy Methyl Methyl
Cellulose
Percent of Original A320
Hours
0
20
40
60
80
100
120
140
160

References

(1) T. P. Dirkse, Chapter 10 in "Characteristics of Separators for Alkaline Silver-Oxide-Zinc Secondary Batteries", edited by J. E. Cooper and A. Fleischer, AF Aero Propulsion Laboratory, Wright-Patterson Air Force Base, Ohio (1964).

(2) (a) E. Weiss, A. J. Salkind and C. G. Oberholzer, Contract NAS-5-2860 (1963), Fourth Quarterly Report. (b) E. Weiss, J. B. Ockerman and C. G. Oberholzer, Ibid., Ibid. Fifth Quarterly Report.

(3) R. F. Amlie and P. Ruetschi, J. Electrochemical Soc., 108, 813-819 (1961)

APPENDIX II

TESTS IN SILVER-ZINC CELLS

by

The Electric Storage Battery Company

TABLE OF CONTENTS

ABSTRACT

A number of separator compositions were tested as components of three plate silver-zinc oxide cells in a standard cycling test. The compositions were in the form of either thin films or envelopes into which the electrodes could be fitted. The electrical cycling was designed to serve as a screening test enabling superior materials to be chosen for more intensive examination. Six materials meet the imposed requirements giving cycling performance superior to cellophane.

I. INTRODUCTION

The Electric Storage Battery Company in this sub-contract to The Borden Chemical Company performed three plate silver zinc battery tests on separator materials developed by Borden under NASA contract NAS5-9107. The testing consisted of cycling in a fixed regime three plate silver-zinc cells containing two layers of the separator being evaluated. The regime included discharge at the 100% depth; 20% overcharge in each cycle, and an accelerated stand test of two weeks at 45°C.

The test procedure was designed to provide a rapid screening test of comparative separator performance. An arbitrary end point was set at ten cycles and those cells completing ten cycles were considered candidates for further and more extensive testing in full cells.

The only commercial separators for alkaline silver cells have been of cellulosic origin, with films of unplasticized cellophane giving the best and most reliable performance characteristics. Unmodified cellulosics are not stable in the battery environment. Both hydrolysis by the electrolyte and oxidation by products of the electrode reactions cause degradation and loss of barrier properties. Very many attempts have been made to modify cellulose films so as to increase their useful lifetime in the system but none have resulted in improvements of the magnitude required.

Recently, however, several films developed in separator programs conducted for NASA by the Borden Chemical Company have been found to have substantially greater resistance to oxidation by silver oxide and to zinc penetration, than unmodified cellulosics. Battery test data on these materials verified the improvement in stability, and greater cycle life was obtained than with similar cells containing cellophane. The present work deals with extensions and modifications of the film compositions previously found in cell testing to have improved separator characteristics. Sample films submitted to ESB for the battery screening test were characterized in the bench screening test program at Borden prior to submission. ESB measured electrical resistance both before and after cell testing and the performance of three plate cells containing the films.

II. SCREENING TEST

A. Electrical Resistance

Separator resistance was measured on each sample prior to cell assembly. The method used and the cell employed are essentially as described in the Cooper-Fleischer Handbook(1). A modification was made in the cell design by adding two fixed platinum sensing electrodes close to the faces of the separator. This leads to greater sensitivity and more reproducible resistance readings. The values measured both as received and after cell testing are given in Table 1. In general, the resistivity decreased after service in the battery.

B. Cell Screening Test

1) Construction (See Figure 3)

a) positive plate - one per cell (1.750" x 1.875" x .030")
wgt. 8.08 g per formed positive plate

(1) Cooper, J. E., Fleischer, A., Battery Separator Screening Methods, AD 447301

b) negative plate - two per cell (1.750" x 1.875" x .045")
wgt. 5.55 g per formed negative plate

c) absorber - a single wrap of Kendall Mills
EM-309 - .0015 in.

d) negative retainer - one layer Viscon - .003"

e) separator - two layers of experimental film
s-wrapped around the positive electrode

f) electrolyte - KOH* - saturated with ZnO
approximately 9 mls are required per cell stack

g) case - $2\frac{9}{16}$" x $1\frac{15}{16}$" x $\frac{11}{16}$"
the 3 plate cell stack is shimmed to fit the internal
dimension of the case

*Percentage concentration of KOH indicated in Table IV.

TABLE 1
Separator Resistivity

Separator	Thickness (in.)		Resistivity			
	Dry	Equilibrated	31% KOH Zinc Saturated		45% KOH Zinc Saturated	
			Initial $\Omega - in^2$	After Cell Failure $\Omega - in^2$	Initial $\Omega - in^2$	After Cell Failure $\Omega - in^2$
193-PUDO	.0009	.0027				
C-3	.0021	.0023	0.019	0.014		
5-9107 -21	.0018	.0020	0.111	0.163		
-22	.0017	.0021	0.042	0.034		
-23	.0018	.0021	0.015	0.010		
-24	.0018	.0022	0.052	0.055		
-25	.0016	.0023	0.025	0.018		
-26	.0013	.0022	0.011	0.005		
-26	.0012	.0019			0.042	0.016
-27	.0013	.0013	0.031	0.028		
-28	.0015	.0016			0.023	0.023
-29	.0018	.0036	0.028	0.030		
-30	.0015	.0028	0.017	0.022		
-31	.0015	.0023			0.033	
-32	.0014	.0023			0.037	
-33	.0008	.0008	0.010			
-23	.0013	.0012			0.149	0.090
563-46	0.006	0.009	-	0.071		
563-47	0.006	0.009	-	0.093		
563-56	0.007	0.007	0.069	0.045		
534-43	0.0055	0.007	0.045	0.045		

The cells were assembled by shimming the stacks to give a standard pack tightness. Cellophane was used as a standard and the cells containing it were built allowing a separator expansion factor of five (the measured expansion factor of cellophane in this electrolyte is three - see Table 1). C-3 film was chosen as a secondary standard and cells containing C-3 and the experimental separators were assembled to the same pack tightness as the cellophane controls.

The cycling regime chosen was designed to provide a rigorous test of the separator. Overcharge at each cycle exposed the samples to oxidizing conditions and caused rapid attainment of complete charge in the negative. Both the repeated overcharge and the fully charged negatives contribute to the formation of dendritic zinc deposits thus promoting penetration of the separator. A charged stand period was included in the test scheme to evaluate this aspect of separator function. This stand test was conducted at 45°C to accelerate any deleterious effects which might occur.

The cycling regime used initially is listed in Table 2. The use of a constant potential charge after the fourth discharge, followed by a c-rate discharge resulted in differing states of charge for some cells during the stand test. The program was therefore modified as shown in Table 3. This change gives more meaning to the calculated capacity stand loss figures.

TABLE 2
Cell Cycling Procedure

1) Using dry charged plates, discharge at C/5 rate to 1.30 volt cut-off
2) Recharge at C/20 rate to 1.2 C
3) Discharge at C/5 rate to 1.30 V cut-off

4) Twice repeat 2 and 3

5) Recharge using modified c.p. at 1.97 V/cell with a current limit of 0.250 amps per cell

6) Discharge at C-rate

7) Recharge at C/20 rate to 1.2C

8) Place cells on charged stand at 45°C for fourteen days

9) Discharge from stand at C/5 rate

19) Repeat steps 2 and 3 for four additional cycles

During the cycling test, cell capacity, voltage, current and temperature were monitored. Failure point was taken as inability to deliver 0.6 of nominal capacity. Cells were run in duplicate and re-checked where early failures occurred.

The capacity values on all cells tested by this regime are listed in Table 4 and depicted graphically in Figure 1. The stand loss data obtained are shown in Figure 2. The cross-hatched areas represent the ampere hours lost during the elevated temperature stand period. An examination of this data indicates a wide variation in the contribution of the various materials to cell capacity retention. Film 5-9107-22 and the combinations of thin films gave the best retention.

TABLE 3

Revised Cycling Procedure

1) Discharge at C/5 rate to 1.30 volt per cell

2) Recharge using constant current mode at C/20 rate to 1.2 times the capacity realized in the previous discharge

3) Discharge at C/5 to 1.30 volt per cell

4) Twice repeat operations 2 and 3

5) Recharge as per 2

6) Discharge at the C-rate to 1.00 volt per cell, then a supplemental discharge at the C/5 rate to 1.30 volt per cell

7) Recharge as per 2

8) Place cells on charged stand at 45°C for fourteen days

9) Discharge cells from stand as per 3

10) Repeat operations 2 and 3

11) Recharge following discharge number seven using a modified c.p. mode limit the voltage to 1.97 volts per cell and the current to 0.250 amp per cell

12) Discharge as per 3

13) Twice repeat operations 2 and 3

In the main, the dry thickness of the materials submitted was close to 1.5 mils. These materials gave varying degrees of resistance to silver diffusion and ability to resist zinc penetration. In order to test out the possibility of including both functions in the separator system, combinations of films were tested. The films were cast at half thickness (0.8 mil) so that the data generated on the combinations could be compared directly to the single films. Combinations were chosen to give a layer to stop silver migration (usually a polyvinyl alcohol film) followed by a layer inert to silver and which had in addition zinc stopping ability. The silver resistant film was in each case placed closest to the silver electrode with the other film interleaved between its two layers. Except in the combination of sample

TABLE 4
Results of Cycling Tests

Ampere-Hour Capacity S-7.5

Separator	Cycle 1	2	3	4	5	6	7	8	9	10
	2.84	1.65	2.00	2.11	1.53	1.85	1.74	1.60	1.10	1.50
C-3	1.95	2.11	2.25	1.80	1.80	*				
	1.86	1.50	1.50	1.80	1.98	1.85	1.86	2.0	2.2	2.5
	1.15	1.70	1.80	*						
5-9107-21	2.16	1.15	1.52	1.75	1.98	1.09	1.49	1.75	1.74	1.68
A 522-62	1.55	1.82	1.12	1.29	1.40	1.17	1.49	1.64	1.76	1.74
5-9107-22	2.24	1.02	1.59	1.86	2.15	2.06	1.49	*		
	2.42	1.23	1.58	1.83	2.45	1.87	2.09	2.34	2.29	2.32
A 522-119	1.93	1.87	2.16	0.26	1.47	1.81	2.02	2.2	2.15	1.98
	2.10	2.12	2.28	2.09	1.35	1.56	1.75	2.13	2.3	2.24
5-9107-23	2.3	2.1	2.3	2.0	*					
A 534-63 M3	2.6	2.1	2.3	1.7	*					
5-9107-24	2.5	2.1	2.2	2.05	1.38	1.17	1.96	2.01	1.68	*
A 534-43 M4	2.5	2.2	2.3	2.17	1.38	1.40	1.44	1.66	1.24	*
5-9107-25	1.58	*								
	1.42	*								
A 504-6 M5	1.71	.78	*							
	2.03	.80	*							
5-9107-26	2.63	1.47	1.93	2.08	1.76	*				
	2.48	1.8	1.75	*						
A Lot 545-18	2.74	2.13	2.18	*						
	2.51	1.96	2.12	*						
5-9107-26	2.5	2.22	2.28	2.21	1.23	1.05	1.15	1.26	1.35	1.37
B Lot 534-24	2.35	2.0	2.14	2.04	1.16	1.05	0.96	0.31	*	
5-9107-27	2.56	1.83	1.48	1.61	1.19	.96	1.03	1.13	1.84	1.96
A 545-64	2.6	1.95	2.23	2.43	1.0	.85	0.9	0.96	1.87	2.1
5-9107-28	2.45	1.79	1.79	1.91	1.4	*				
B 545-116	2.57	*								
5-9107-23	1.88	1.67	1.84	1.69	0.89	0.91	1.0	1.13	1.27	1.53
B 534-63	2.62	2.26	2.25	2.14	1.12	1.17	1.29	1.46	1.65	2.01
5-9107-29	2.55	2.24	2.20	2.17	2.42	1.74	1.75	1.66	1.86	1.72
A 563-101	2.52	1.89	1.92	1.89	2.13	1.64	1.41	-	1.84	1.65

TABLE 4 continued

BORDEN 115362

	Ampere Hours 1	2	3	4	5	6	7	8	9	10
5-9107-30 A 563-115	2.46 / 1.93	1.94 / 1.75	1.90 / 1.75	2.06 / 1.97	2.25 / 2.21	1.67 / 1.70	1.40 / 1.53	- / 1.83	- / 1.82	
C-3 A	2.44 / 2.50	2.08 / 2.02	2.17 / 2.08	2.28 / 2.15	2.42 / 2.43	1.72 / 1.37	1.65 / 1.01	- / 1.58	1.67 / 1.78	1.80 / 1.84
5-9107-32 B 563-157	2.01 / 2.03	1.8 / 2.03	0.74 / 1.66	* / 1.82	- / 1.73	- / 1.53	- / 1.37			
5-9107-31 B 563-156	2.37 / 2.45	0.98 / 2.14	* / 2.10	- / 2.03	- / 2.03					
A C-3/59107-33 A	2.45 / 2.45	1.82 / 1.77	2.08 / 2.14	1.95 / 2.10	1.88 / 1.32	0.88 / 1.55	0.74 / 2.03	.93 / 1.51	1.04 / 1.91	1.23 / 1.91
5-9107-22 A 5-9107-29 A	2.38 / 2.45	1.91 / 1.56	2.1 / 2.2	1.4 / 1.92	* / .65					
5-9107-27 A 5-9107-30	2.39 / 1.65	2.02 / 1.73	2.12 / 2.08	2.2 / 2.35	2.0 / 2.04	1.50 / 1.69	1.79 / 1.92	1.31 / 1.52	1.66 / 1.63	1.65 / 1.83
A C-3/59107-29	2.17 / 2.45	1.94 / 2.0	1.83 / 1.83	1.91 / 2.00	1.95 / 1.88	1.61 / 1.59	1.83 / 1.96	1.63 / 2.15	1.96 / 1.44	2.12 / 1.68
5-9107-23 A 5-9107-29 A	2.38 / 2.35	1.94 / 1.94	1.97 / 1.92	1.91 / 1.91	2.03 / 1.95	1.63 / 1.58	1.84 / 1.78	1.88 / 1.93	.83 / 1.49	1.20 / 1.84
5-9107-22 A 5-9107-30 A	1.79 / 2.3	1.77 / 1.09	1.86 / 0.96	1.94 / 0.98	2.03 / 0.98	1.79 / *	1.96 / *	*		
PUDO 193 Δ)	2.34	2.25	2.50	2.15	1.71	1.52	*			

Notes

1) * Indicates cell short and removal from test.

2) A - Cells contain 31% KOH which has been saturated with ZnO.

3) B - Cells contain 45% KOH which has been saturated with ZnO.

4) Δ - Cell capacity reported is the average of 5 cells. All cells shorted on recharge following discharge 6.

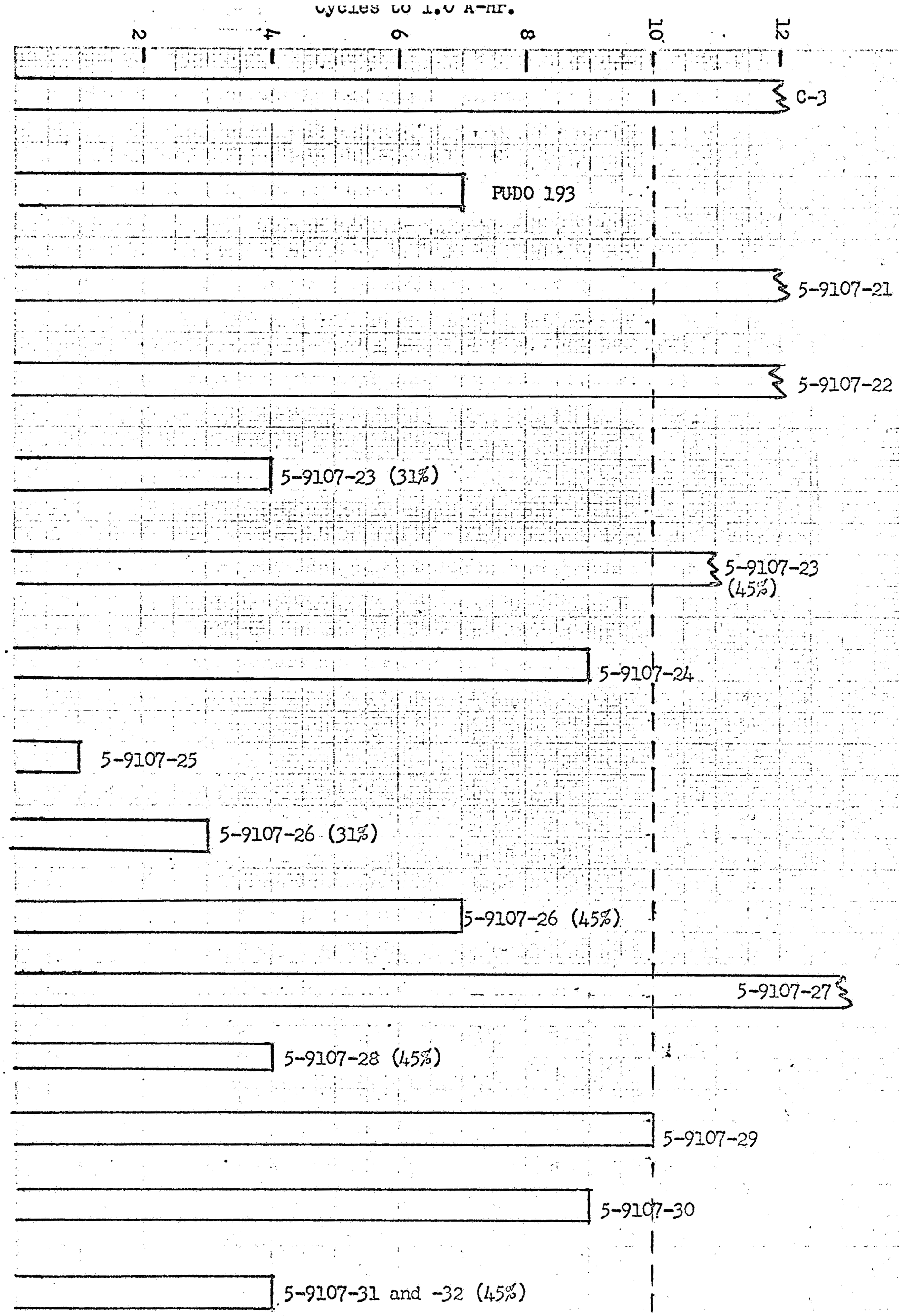
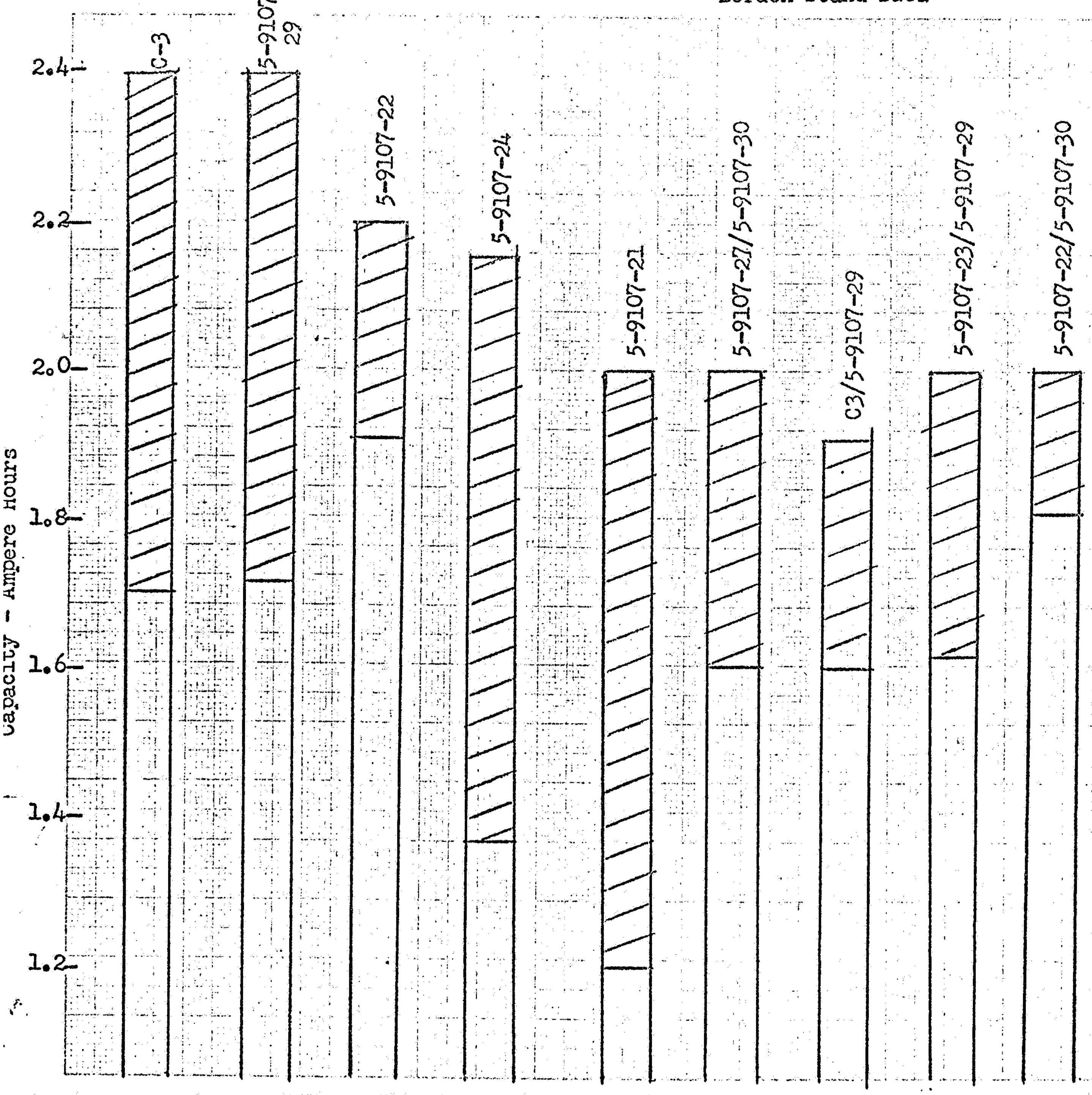


Figure 1
Borden Cycling Data

Figure 2
Borden Stand Data



Oross hatched area indicates capacity loss during charged stand time period of two weeks at 45° C.

31% KOH

5-9107-22 with pva, all of the combinations performed well in both cycle and stand tests. The failure of the two combinations containing 5-9107-22 is not readily explainable since the individual films were each superior to the combination.

C. Pressure Cell

In the initial studies under this contract, it was proposed that the electrochemical evaluation be conducted in a lucite cell so constructed that controlled tension can be placed on the cell stack by the use of springs. Micrometer measurements provide a precise measurement of cell expansion and contraction against the restraining force of the springs. The cell is 4 7/8 in. x 5 11/32 in. inside dimensions, with facing plates 2 1/2 in. x 3 3/4 in. x 0 to 0.25 in. variable thickness. A rubber gasket divides the cell into two compartments and provides a seal against electrolyte. The cell is shown in Figure 4. Using conventional wrapping technique, early failures by shorting were experienced with both cellophane PUDO 193 and C-3 separation, non exceeding six cycles. All failures were due to zinc treeing through the separator. The major contributing cause appeared to be excessive washing of the negative active material resulting from the high ratio of electrolyte to active material volume. Much of the zinc electrode became dislodged and fell to the bottom of the cell. To prevent this loss of material the separator materials were coated onto Viscon paper and formed by Borden into envelopes open on one end (in the case of material 563-56 the envelope was unsupported). The zinc plates were inserted into the envelopes and the cycling regime applied. In these tests the central positive plate was wrapped in a layer of dynel and a single layer of either C-3 or PUDO 193, while both negative plates were enclosed by separator envelopes. The capacity data obtained is given in Table 5. In all tests zinc saturated 31% KOH served as electrolyte.

TABLE 5

Ampere-Hour Capacity

Separator Envelopes Tested in the Pressure Cell

Separator Envelope	Positive Wrap	Discharge # 1	2	3	4	5	6	7	8	9	10
545-65	None	2.55 / 2.63	2.13 / 2.07	2.08 / 1.95	2.06 / 1.97	1.02 / 1.18	0.7 / 1.0	* / 1.09			
545-65	PUDO 193	2.45	1.49	1.65	1.88	1.65	2.54	2.04	1.96	1.90	1.67
545-65	C-3	2.51	1.45	1.60	1.83	1.13	1.47	1.71	1.92	2.0	1.85
563-46	C-3	2.43 / 2.18	2.09 / 2.16	1.92 / 2.06	1.89 / 2.0	1.88 / 2.06	0.75 / 1.65	0.78 / 1.66	* / 1.58	-- / 1.47	-- / 1.16
563-47	C-3	2.39 / 2.32	1.96 / 1.09	2.0 / 1.22	2.04 / 1.37	2.13 / 1.76	1.05 / 1.68	* / 1.75	-- / 1.46	-- / 0.99	-- / 0.86
563-56	C-3	2.56 / 2.27	1.97 / 2.35	1.83 / 2.22	1.57 / 2.15	1.43 / 2.22	0.48 / *	0.61 / --	* / *		

* Shorted cell

Since the major effort in the contract was devoted to evaluation of film type separators, the time allotted to envelope evaluation was necessarily restricted. Thus the results obtained are not definitive and the effects of several parameters of the test on the results were not examined, e.g., quantity of electrolyte, pressure on the stack, thickness of envelope, etc. Even so, two of the compositions 545-65 and 563-46 met the test requirements of ten cycles.

The total equilibrated thickness of separator layers in the envelope testing is two to four times that tested in the other part of the program. This combined with the other features of the test make comparisons between the two set-ups (films and envelopes) of doubtful validity. Attempts to make envelopes which could be fitted into the more conventional cell set-up and thus provide direct comparison were not successful.

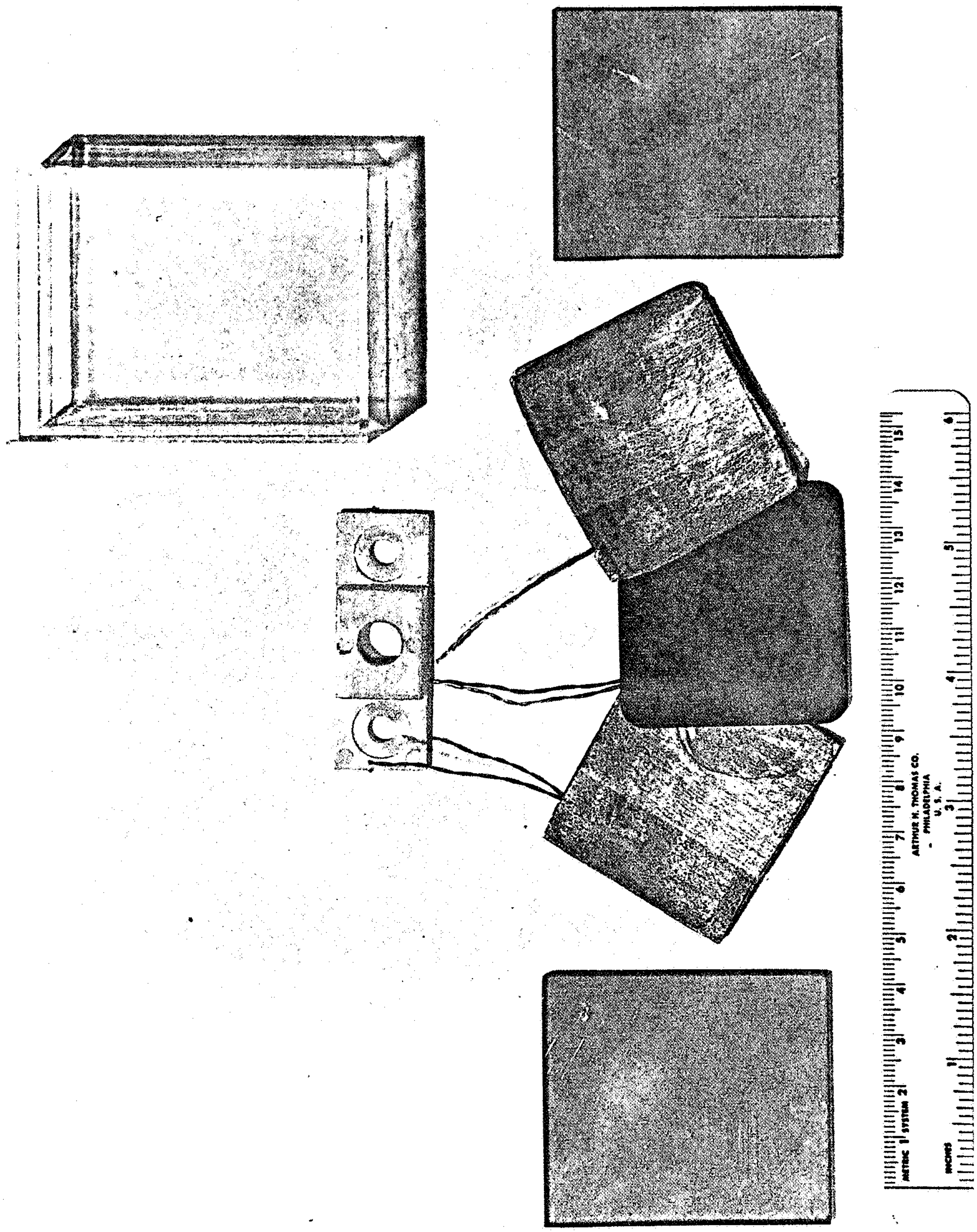
In summary then, the concept of the use of separator envelopes in place of multi-wraps of separator film was not explored in sufficient depth in this work to provide an unequivocal comparison. Additional work is needed to assess their usefulness.

Failure Analysis

An analysis of the cells after failure has shown two distinct mechanisms of failure. Where failure occurred within the first few cycles, silver penetration appeared to be the primary cause. Where failure occurred in the later cycles, zinc shorting could be assigned the major blame but with silver penetration a contributing factor.

CONCLUSIONS

On the basis of the test data generated, it is recommended that samples 5-9107-21, 5-9107-22, 5-9107-27 and 5-9107-29 be chosen for evaluation in full cells. Combinations of C-3 with 5-9107-29, 5-9107-27 and 30, C-3 with 5-9107-33 and 5-9107-23 and 29 also deserve to be more fully evaluated.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